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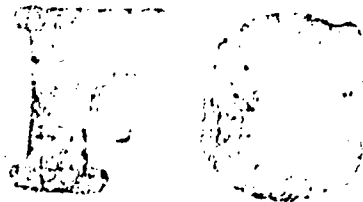
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WADC TECHNICAL REPORT 51-325

PART 2



**RESEARCH FOR LOW-APPLICATION-TEMPERATURE,
ELECTRICALLY CONDUCTING, TRANSPARENT COATINGS
FOR AIRCRAFT WINDSHIELDS AND RELATED COMPONENTS**

PAUL SCHALL, JR.

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WRIGHT AIR DEVELOPMENT CENTER

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MARCH 1956

**MATERIALS LABORATORY
CONTRACT No. AF 33(616)-2467
PROJECT No. 7312
TASK No. 73125**

**WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

FOREWORD

This report was prepared by the Battelle Memorial Institute under USAF Contract No. AF 33(616)-2467. The contract was initiated under Project No. 7312 "Finishes and Materials Preservation", Task No. 73125 "Transparent Conducting Coatings for Aircraft Materials", formerly RDO-616-13, "Optical Coatings for Aircraft Materials", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with J. R. Cannon acting as project engineer.

The present project, aimed at fulfilling the objectives outlined above, is a continuation of the work done at Battelle on Contract No. AF 33(616)-342, and reported in Wright Air Development Center Technical Report 54-325.

This report covers work conducted from June 1954 to August 1955.

ABSTRACT

Transparent, conducting films of indium oxide on glass were prepared by thermal oxidation (at 250 to 400 F) of evaporated and sputtered indium films. Addition of tin to the films decreased their electrical resistance. Tin-doped films were prepared with resistance as low as 50 ohms per square and with optical transmittance of 75 to 80 per cent. The films are photoconductive. However, for the low resistance films (less than 100 ohms per square) the resistance changes only a few per cent when the films are light-dark cycled.

The temperature coefficient of resistance of the films is less than +0.04 per cent per degree (F).

Stability tests were conducted on the films under load (up to 1500 watts per square foot) and without load over a wide range of temperatures. Film resistance changes are less than 20 per cent in 150 hours.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



R. W. CONNERS
Lt Colonel, USAF
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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
SUMMARY AND CONCLUSIONS	1
DISCUSSION	3
Evaporation and Thermal Oxidation of Indium Films	3
Undoped In-O Films	3
Sputtering and Thermal Oxidation of Indium Films	14
Sputtering Conditions	14
Conversion of Sputtered Indium Films	16
Impurity Additions to Sputtered Indium Films	17
The Effect of Magnesium Fluoride Antireflecting Layers on the Reflectivity of In-O Films	22
Thermal and Electrical Characteristics of In-O and In-Sn-O Films	24
Temperature Coefficient of Resistance	26
Environmental and Load Tests of In-Sn-O Films	26
Fundamental Studies	32
Thickness Measurements	32
Diffraction Studies	34
Electron Microscopy Studies	34
Recommendations	35
EXPERIMENTAL DETAILS	36
Materials	36
Dual Evaporation Source	36
Oxidation Apparatus for Evaporated Films	38
Resistance Stability Tests on Evaporated Films	38
Sputtering Apparatus and Conditions	38
Temperature Measurements During Sputtering	39
Thermal Conversion of Sputtered Films	41
Application of Sb-O Undercoating and Overcoating	41
Application of Magnesium Fluoride Overcoating to In-O Films	43
Measurement of Temperature Coefficient of Resistance	44
Electrical Load Tests	44
APPENDIX	
LITERATURE SURVEY, BIBLIOGRAPHY, AND REVIEW OF INVESTIGATIONS AT BATTELLE AND BALCO.	45
Literature Survey	45
Patents	45
Other Technical Literature	47
Bibliography	52
Patents	52
Other Technical Literature	54
Review of Investigations at Battelle and Balco	55
Deposition of Films From Solution	56
Deposition of Films by Evaporation and Sputtering	58

INTRODUCTION

In the interest of promoting flight safety, a transparent, high-conductivity coating is required for the removal, by electrical heating, of fog, frost, and ice formations on the interior and exterior areas of glass windshields and side panels of aircraft. This coating must have a resistance no greater than 100 ohms per square. Quarter-inch plate glass coated on one side must have a light transmittance of at least 85 per cent and a haze value no greater than 1 per cent. The coating must be capable of dissipating 1500 watts per square foot to a moving air stream. The coating must be applicable to precision-ground laminated glass at temperatures below 250 F, the bubbling temperature of the plastic laminating material.

SUMMARY AND CONCLUSIONS

Indium oxide films were formed by evaporation of indium in oxygen at pressures from 0.25 to 4 microns and subsequent thermal oxidation at temperatures of 250 to 400 F. It was found that the oxygen pressure during evaporation must be less than about 1 micron to obtain films with good resistance stability. In-O films were prepared with resistance in the range 200 to 6000 ohms per square and with optical transmittance of 75 to 80 per cent. The photoconductivity effect, discussed in Wright Air Development Center Technical Report 54-325, was much smaller in the low-resistance films than in the high-resistance films.

Considerable improvement in In-O films prepared by the evaporation-conversion process was effected by addition of tin to the film by simultaneous evaporation. Tin-doped films were prepared with resistance as low as 50 ohms per square and with optical transmittance of 75 to 80 per cent. These values are in the neighborhood of the values required by the contract, that is, 100 ohms per square and 85 per cent transmittance. Resistance stability of the tin-doped films was better than that of undoped In-O films. In the case of low-resistance tin-doped films (less than 100 ohms per square), resistance changed only a few per cent as a result of light-dark cycling (photoconductivity effect).

Investigations of sputtering parameters for preparation of indium films resulted in better control of the entire process. However, the best In-O films made by sputtering had a resistance of about 500 ohms per

squares with transmittance of 75 to 80 per cent. Control of the gas pressure, gas composition, and sputtering current were the most important factors in improving the process.

Three methods of conversion were studied for sputtered indium films, namely, (1) conversion in an oven at atmospheric pressure, (2) load heating at low pressure, and (3) oven heating at low pressure. The oven-heating method at low pressure is the most rapid method of conversion. However, it also is the most difficult to control.

Antimony was added to In-O films by three methods: (1) sputtering an indium film on an antimony oxide undercoat previously applied to the glass, (2) overcoating In-O films by hydrolyzing an antimony salt in situ, and (3) simultaneous sputtering of indium and antimony from an InSb cathode. None of these methods gave films of lower resistance than that of In-O films previously prepared.

Tin doping reduced the resistance of the In-O films made by the sputtering process, as was the case for films made by the evaporation method. Films with resistance as low as 250 ohms per square and with transmittance of 70 per cent were obtained.

A study was made of the effect of overcoating In-O films with MgF_2 to decrease reflectivity and thereby increase optical transmission. Increases in transmission as high as 10 per cent were obtained.

Stability tests were made on In-O and In-Sn-O films under load as well as under various environmental conditions. Load tests were conducted with the film in the air stream of a blower. Because of glass breakage above 120 F, it was necessary to control power dissipation so that the average plate temperature did not rise above 120 F. When a power of 1500 watts per square foot was dissipated, it was necessary to control the power thermostatically with an off-on cycle so that the current was applied for about 1/3 of the time. Tests also were made with continuous power of about 500 watts per square foot. This method maintained a plate temperature of 120 F in the stream of air which was used. Under both of the above conditions and in still air at 288 F, resistance changes of less than 20 per cent were generally observed in 150 hours of test. In many cases, resistances were noted to be decreasing at the end of the test after an initial increase.

Temperature coefficients of resistance were generally less than +0.04 per cent per degree Fahrenheit. The photoeffect and irreversible changes during temperature cycling partially obscured the true T. C. values in many cases. No detrimental effects of temperature cycling from -90 F to +250 F were noted.

A fundamental investigation was carried out on several In-O films prepared by the evaporation-conversion and sputtering-conversion

processes and by high-temperature spraying, in an attempt to correlate film properties with structure and processing conditions. Film resistances ranged from 105 to 2100 ohms per square. It was found that the differences in resistance were a result of differences in resistivity rather than in film thickness. No correlation was found between film structure (as determined by electron microscopy and X-ray and electron diffraction) and the properties and processing conditions of the films.

DISCUSSION

Indium oxide films were prepared by evaporation and sputtering of metallic indium, followed by thermal conversion to the oxide. The effects of additions of antimony and tin to the films and of overcoating with MgF_2 were studied. Stability tests and structure studies were carried out on these films. The results of the investigation are described in the following pages.

Evaporation and Thermal Oxidation of Indium Films

Undoped In-O Films

In previous work at Battelle on Contract No. AF 33(616)-342 (Wright Air Development Center Technical Report 54-325), indium films evaporated at an air pressure of about 6 microns of mercury were converted to the oxide by heating to 250 F. Transparent films produced by this method had a resistance as low as 300 ohms per square in vacuum. However, when these films were exposed to normal atmosphere, large (several orders of magnitude) increases in resistance occurred. Subsequently, information was obtained through personal contact with workers in Europe that indium films evaporated in an oxygen atmosphere at a pressure of 10^{-4} to 10^{-3} mm of mercury yield transparent, conducting films with stable resistances when thermally oxidized in air at about 300 F. The information indicated that, to obtain films having a resistance of 100 ohms per square or less, multiple-layer films would be necessary.

In view of the above information, a study was made of the evaporation of indium in oxygen. To maintain various oxygen pressures during the deposition of indium, a variable leak was installed in the vacuum evaporator. A series of indium films was prepared using oxygen pressures in the range 0.5 to 4.0 microns of mercury. In the previous work, slow evaporation rates and longer source-to-substrate distances (15 cm) were found to result in films that were oxidized more easily. Accordingly, a 15-cm source-to-substrate distance was used in the present work, together with

an evaporation rate such that a film having a resistance of about 1000 ohms per square was deposited in 30 minutes or longer. Metal films having a resistance of 2000 ohms per square or less were subjected to oxidation treatment by load heating* in the vacuum system, using an oxygen pressure of 10 to 20 microns and a temperature of 250 F. Films having a resistance higher than 2000 ohms per square were heated in air in a constant-temperature oven. One high-resistance film (4600 ohms) was oxidized by load heating, but the glass plate cracked as a result of local thermal gradients.

It was found that films made at the higher oxygen pressures have higher resistance than those made at lower pressures. Also, they convert to In-O films with higher resistance. However, films made at the higher pressures convert more readily. In addition, it was found that indium films evaporated in oxygen at 1 micron and in air at 6 microns convert to In-O films of comparable resistance, as would be expected, since the oxygen pressure is about the same in both cases. However, the oxygen-evaporated In-O films were more stable. Upon aging for several days at room temperature, the oxygen-evaporated In-O films prepared during this early work increased in resistance by a factor of 2 to 4, compared with 2 to 3 orders of magnitude for the air-evaporated In-O films discussed in Wright Air Development Center Technical Report 54-325.

The results of the preliminary work described above indicated that oxygen-evaporated films should be prepared at a pressure of not more than 1 micron.

Subsequently, films of various thicknesses were made at various oxygen pressures in the range 0.25 to 1 micron, to determine the maximum thickness of indium which could be thermally oxidized at 250 F, and to compare the resistance stability of films made at various oxygen pressures. Evaporation conditions other than pressure were the same as described above, i. e., source-to-substrate distance was 15 cm, and the evaporation rate was such that a film having a resistance of 1000 ohms was formed in a period of 30 minutes or longer. The substrate temperature was about 100-120 F.

Indium films having resistances from 1000 to 10,000 ohms per square were evaporated and oxidized in an oven at 250 F. It was found that the resistance of the metal film should not be lower than about 5,000 ohms per square to permit oxidation at 250 F. The 5000 ohms-per-square metal films were converted to oxide films having light transmittance of 70-80 per cent and minimum resistance** in the range 420-650 ohms per square. In general, for metal films having a resistance of 5,000 ohms per square or greater, the resistance of the resulting oxide films was about one order of

*The terms "load heated" and "load heating" will be used to designate heating by passing an electrical current through the films.

**Minimum resistances were obtained either by warming the oxide films in vacuum or by exposure to light. As will be discussed later in this report, both of these procedures result in reducing film resistance to the same low value.

magnitude lower than the resistance of the metal films. The films were sufficiently oxidized in 2 to 3 days at 250 F to have a light transmittance of 70-80 per cent. The films formed at the higher pressures (in the range 0.25 to 1 micron) were slightly easier to oxidize.

Two attempts were made to reduce resistance by formation of double-layer films. It was hoped that the second layer might have lower resistivity than the first, as a result of the influence of the indium oxide substrate on orientation and grain size of the second indium layer. The procedure used to form the double-layer films was to place a glass plate coated with indium oxide and an uncoated glass plate at equal distances from the evaporation source. The resistance of the indium deposited on the uncoated glass slide was then measured continuously during the evaporation period to duplicate, as closely as possible, the evaporation conditions used in evaporating the first layer of material.

The first double-layer film had a resistance of 630 ohms per square and a light transmittance of 80 per cent prior to deposition of the second layer. After the second layer was deposited and oxidized at 250 F, film resistance was 516 ohms per square and light transmittance was 72 per cent. These values are to be compared with a resistance of 550 ohms per square and light transmittance of 80 per cent for the single-layer film made simultaneously with the second layer of the double-layer film. The other double-layer film was formed by depositing a second layer on a film having a resistance of 470 ohms per square and 80 per cent light transmission. The values for the double-layer film and for the single-layer film made simultaneously with the second layer are 257 ohms per square and 75 per cent light transmittance, and 464 ohms per square and 80 per cent light transmittance, respectively.

It appears, from the work with double-layer films, that the resistivity of the second indium oxide layer is not significantly lower than that of the first layer, and that reducing the resistance to 100 ohms per square by increasing thickness will result in formation of films having a light transmission too low for the intended use of the film.

Since it appeared probable that the desired optical properties could not be obtained in conjunction with the desired electrical properties with In-O films prepared at 250 F, it was decided to investigate other means of lowering the resistivity of the films. Two possible methods for achieving this goal are addition of impurities to the film and use of oxidation temperatures somewhat higher than 250 F.

Although the goal of this investigation was to develop a film having a maximum application temperature of 250 F, it was thought desirable to determine the effect of oxidation temperature on film properties. A number of indium films were evaporated, using the same evaporation conditions as were used for films which were oxidized at 250 F. The resistance of these indium films was 5,000 ohms per square prior to oxidation treatment

at 300 F. The first few films were left in the oxidation oven for about 24 hours. At the end of this oxidation treatment the films had good transparency (80-85 per cent transmittance of white light); however, film resistance was of the order of 100 kilohms per square. To determine the cause of this high film resistance, facilities were installed in the oven to permit resistance measurements during the oxidation treatment. It was found that similar indium films reached a minimum resistance of about 400 ohms per square in periods of 10 to 50 minutes. The resistance remained constant for 1/2 to 1 hour, and then began to increase, attaining values as great as 100 kilohms per square in one day, with no evidence that the films were approaching a stable high resistance. Films which were removed from the oven as soon as they attained the minimum resistance value had a light transmittance of about 50 per cent. Films left in the oven until resistance again began to increase had a light transmittance of about 70-75 per cent.

To study these changes in film properties more thoroughly, a small furnace was constructed to allow both transmission and resistance measurements to be made continuously during the oxidation treatment. Using this apparatus, the time required for oxidation was much longer (an average of about 3 hours as compared to an average of 1/2 hour when oxidation was carried out in the oven) although the temperature was the same in both cases. The reason for this difference in behavior is not known. With the exception of the difference in time requirement, the film behavior was similar, using both heating devices. At 300 F, metal films having a resistance of 5000 ohms per square were converted to oxide films having resistance in the range 220-600 ohms per square and light transmittance of 70-80 per cent. The above resistance values are the minimum values attained during the oxidation treatment. Table 1 shows the results for the best films made from 5000 ohms-per-square metal films, using oxidation temperatures of 250 and 300 F.

As can be seen in Table 1, lower resistances were obtained at 300 F than at 250 F. However, only a slight improvement in light transmission was obtained at the higher temperature. Another point of interest is the behavior of the three pairs of films, 9507-66 and 9507-66A, 9507-70 and 9507-70A, and 9507-80 and 9507-80A, oxidized at 300 F. The two films of each pair were evaporated simultaneously, and the "A" film was subjected to prolonged oxidation (accompanied by a resistance increase), whereas oxidation of the other member of the pair was stopped at the minimum resistance value. Immediately after oxidation, the "A" film of each pair had a much higher resistance. The greatest difference occurred between 9507-66 and 9507-66A. Film 9507-66A had a resistance about tenfold greater than that of 9507-66. However, the difference in minimum resistance (after exposure to light) was much smaller in each case than the difference immediately after oxidation. Thus, the resistance increase on prolonged oxidation does not appear to be due to permanent structural or compositional changes.

TABLE 1. RESISTANCE AND LIGHT TRANSMITTANCE OF In-O FILMS
FORMED BY OXIDATION AT 250 AND 300 F

Film	Oxidation Temperature, F	Minimum Resistance ^(a) , ohms per square	Transmittance of White Light, per cent
9507-46	250	420	70
-48	250	465	70
-29	250	470	70
-45	250	550	80
-31	250	1730	75
-70	300	220	72
-70A	300	225	75
-78	300	260	72
-80	300	295	75
-80A	300	330	75
-66	300	370	70
-66A	300	590	80

(a) These resistances are the minimum values obtained under illumination. The effect of illumination on film resistance is discussed later.

The films listed in Table 1 are not representative of all the films made from 5000 ohms-per-square metal films, but are the best films which had been obtained under the specified oxidation treatments at this point in the investigation. Other 5000 ohms-per-square metal films yielded In-O films having minimum resistance as high as 2000 ohms per square. Also, some similar films were much more difficult to oxidize. It should be pointed out, however, that the films whose properties differed greatly from those shown in Table 1 were in the minority, and, in many cases, the deviations could be attributed to differences in evaporation rate. The important effects of evaporation rate on ease of oxidation and the properties of the resulting In-O films had been recognized previously. However, during the course of the work it became increasingly evident that the initial evaporation rate, i.e., the rate at which the first molecular layers of indium are deposited, is extremely important.

The procedure which was used to evaporate indium was to increase the power input to the evaporation source until evaporation began, as evidenced by a change in resistance between the bus bars on the glass slide being coated. In some cases the power input was slightly too high and was adjusted downward as soon as it was determined, from the rate of change of resistance, that the evaporation was too rapid. Although this adjustment was generally made in the first 30 seconds of the evaporation (over-all evaporation time was 30 minutes or longer), films made with a higher initial evaporation rate were generally more difficult to oxidize and yielded In-O films of higher resistance. Therefore, a new evaporation holder was constructed which permitted accurate temperature measurements of the evaporating material to be made, thereby obtaining more precise control over evaporation rate, particularly the initial rate. With this holder, reproducibility of results was greatly improved.

As was discussed previously, lowest resistances of In-O films are obtained in vacuum. The films undergo resistance increases when exposed to air, and their resistance also changes with illumination. It was found, in testing several films, that the same low resistance as is obtained in vacuum is also obtained on prolonged (24-hour) illumination. This lowest value obtained is referred to as the "minimum resistance" in this report.

A light-tight airtight box was constructed for use in studying the effects of environment and illumination on film resistance. The apparatus and procedure used for this study are described in the Experimental Details section. The films were light-dark cycled in both dry (in the presence of a desiccant) and humid air (100 per cent relative humidity) at room temperature. Films which increased in resistance after several days' exposure to air were exposed to light from two 15-watt fluorescent lamps at a distance of about 2 inches.

The following observations were made on films oxidized at both 250 and 300 F. The films attained a stable low resistance in about 24 hours of illumination with about 75 per cent of the resistance decrease occurring in

the first hour. The rate of resistance increase during the dark portion of the cycle was much lower than the rate of decrease under illumination. No tendency to approach a stable higher resistance was observed even after 14 days in the dark. Films were subjected to as many as five light-dark cycles in both dry and humid air. There was no noticeable difference between the behavior in dry and humid atmospheres. Films oxidized at 250 F exhibited an increase in the minimum resistance attained under illumination with each successive cycle. For example, a group of six films oxidized at 250 F had minimum resistance, after the fifth light cycle, 63 to 113 per cent higher than the minima at the end of the first light cycle. This seems to indicate the occurrence of some permanent structural or compositional change in the films during the test period. It is not known whether this change is the direct result of the strong illumination to which the films were subjected, or if it is a change which would occur with time under any aging conditions.

The data on films oxidized at 300 F are more limited; the greatest number of light-dark cycles to which any of these films was subjected was three. The minimum resistance at the end of the third light cycle was in no case more than 10 per cent higher than the value obtained after the first light cycle. Values for films oxidized at 250 F had increased 30 to 80 per cent at the same stage in the test procedure.

Another comparison among the various films can be made by considering the percentage increase in resistance attained during the first day and the first 5 days in the dark, after the films had reached the minimum resistance under illumination. This comparison is given in Table 2.

Although the ranges of values for the percentage increase of resistance overlap for films oxidized at 250 and 300 F, the use of the higher temperature resulted in some improvement in resistance stability. There does not seem to be any good explanation for the variation in resistance stability of the films oxidized at 250 F. However, in the case of the films oxidized at 300 F, the film with the least stable resistance, 9507-66A, was evaporated simultaneously with the film having the most stable resistance, 9507-66. In this case, as has been discussed in a previous section, 9507-66A was subjected to prolonged oxidation treatment and attained a high resistance during oxidation, whereas 9507-66 was removed from the oxidation oven at the minimum resistance value. The reason why prolonged oxidation affects resistance stability in this manner is unknown.

It is known that the resistance of In-O films prepared by spraying at high temperatures can be lowered by addition of tin. To study the effect of tin doping on In-O films prepared by the evaporation-conversion process, several films were prepared by evaporating the two metals simultaneously, and subsequently converting them in air at 300 and at 400 F. The dual evaporation source used for preparing the In-Sn films is described in the "Experimental Details". This source permits the temperatures of the tin and indium to be controlled independently. Source temperatures were

TABLE 2. RESISTANCE INCREASE OF In-O FILMS
DURING STORAGE IN THE DARK

Film	Oxidation Temperature, F	Minimum(a) Resistance, ohms per square	Increase in Resistance After 1 Day in Dark, per cent	Increase in Resistance After 5 Days in Dark, per cent
9507-40A	250	516	54(b)	184
-48	250	464	44(b)	190
-25	250	1015	40(c)	--
-46	250	419	31(b)	118
-43	250	461	26(b)	80
-45	250	550	23(b)	67
-42A	250	257	20(b)	62
-29	250	501	16(c)	--
-66A	300	592	31(c)	75
-70	300	220	16(c)	35
-70A	300	224	15(c)	41
-66	300	373	11(c)	18

(a) These are the lowest resistances attained in the first light cycle.

(b) Average for five cycles.

(c) Average for three cycles.

chosen to give films containing 10 per cent tin by weight.* Accurate temperature control was difficult, because of recurrent shorting of the thermocouples used to measure the temperatures, and because the source has a high heat capacity, so that the temperatures do not respond rapidly to changes in the heater currents. However, in spite of these control difficulties, spectrographic analysis of one film (131-29) showed the tin content to be 10.2 ± 0.5 per cent by weight, in remarkable agreement with the desired value of 10 per cent.

For the first four In-Sn films which were made, the tin evaporation was started slightly before the indium evaporation. After oxidation, the films thus prepared had high resistance. Consequently, for subsequent films, the indium evaporation was started first. Films prepared this way had much lower resistance. The properties of some In-Sn-O films are given in Table 3. Of the films for which the indium evaporation was started first, most had a resistance of 100 ohms per square or less after the first exposure to light, and an optical transmittance of about 80 per cent. Two films had high resistances, 195 and 200 ohms per square; however, the transmittances also were high, 87 and 89 per cent, respectively.

The stability of the In-Sn-O films appears to be better than that of the undoped In-O films. The greatest deviation of the second minimum resistance from the first, for the films listed in Table 3, is 14 per cent. However, this improved stability may be a result of the lower resistance of the doped films. It had been observed previously that high-resistance films are more unstable than films of lower resistance.

Figure 1 illustrates the effect of adding tin to the In-O films. The figure is a graph of resistance (after the first exposure to light) and optical transmission for several undoped and tin-doped films. A "good" film, that is, one with low resistance and high transmission, should be near the lower right corner of the graph. It is clear that addition of tin effected a considerable improvement in the films.

A few films were prepared with nominal** tin contents of 1 and 5 per cent. The results are not conclusive, but it appeared that the optimum tin concentration is greater than 1 per cent.

One film (10 per cent tin) was prepared on Gafite plastic. The film had a resistance of 276 ohms per square and transmittance of 75 per cent after conversion. However, the film was crazed and non-adherent.

*The temperatures (690 C for In and 760 C for Sn) were calculated from data given by S. Dushman, Scientific Foundations of Vacuum Technique, John Wiley and Sons, Inc., New York (1949), pp 738-9.

**Assumed, from evaporation source temperatures.

TABLE 3. PRODUCTION CONDITIONS AND PROPERTIES OF In-Sn-O FILMS

Film	Evaporation Time, min	Oxidation Temperature, F	Optical Transmission, per cent	Minimum Resistance, ohms per square	Resistance After About One Week in Dark, ohms per square	Second Minimum Resistance, ohms per square
131-20(1)	--	300	78	500	848	682
-20(1)	--	300	77	600	844	632
-24(1)	95	300	80	4500	8730	4930
-24(1)	95	300	83	3600	7930	3920
-29	100	300	81	105	--	--
-29A	100	300	82	97	115	108
-32	91	300	87	195	283	189
-32A	91	300	89	200	226	189
-37	102	400	80	77	80	74
-37A	102	300	79	82	85	78
-60	128	400	74-78	76	84	65
-60A	128	400(2)	76-83	70	80	66
-64A	118	400(2)	79-81	61	64	55
-71	151	300	74-78	66	76	66
-75	129	400(2)	78-81	68	76	62
-84	102	400(2)	75-78	50	50	48
-90	120	400(2)	72.5-78	88	94	86

(1) Tin evaporation started first.

(2) Conversion was started at 300 F but changed to 400 F to speed conversion.

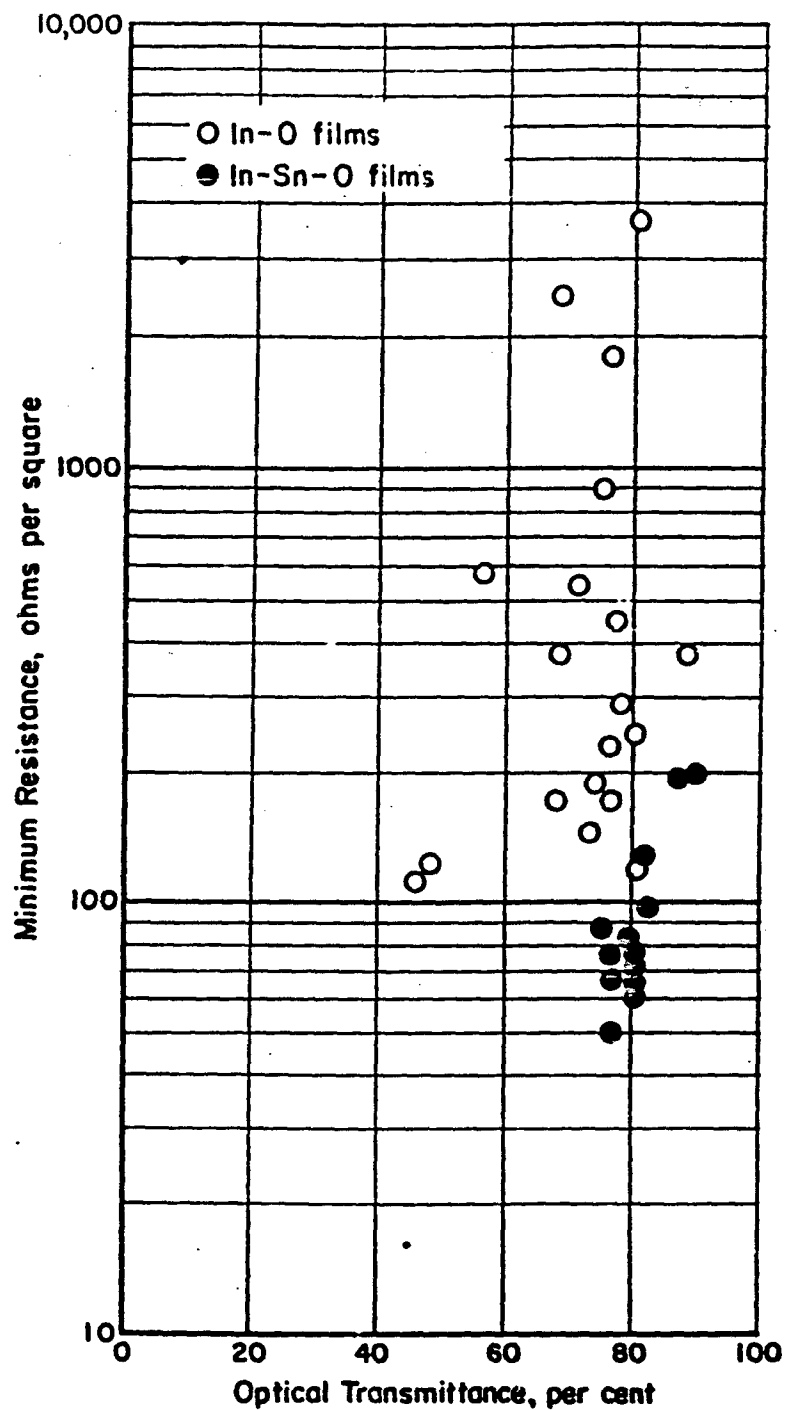


FIGURE 1. RESISTANCE AND OPTICAL TRANSMITTANCE OF UNDOPED AND TIN-DOPED In-O FILMS PRODUCED BY THE EVAPORATION-CONVERSION PROCESS

A-16673

Sputtering and Thermal
Oxidation of Indium Films

Sputtering Conditions

Preliminary studies on the preparation of indium films by sputtering and on conversion of the films to the oxide were carried out at Battelle under Contract No. AF 33(616)-342 (Wright Air Development Center Technical Report 54-325). On the present project, initial effort was directed toward deriving a set of sputtering conditions such that indium films with reproducible characteristics could be produced.

In the early work, there was considerable instability in the discharge; that is, the current was unstable, and the glow discharge moved from place to place in the bell jar. Furthermore, in some cases the films produced had extremely high resistance (greater than 10 megohms per square), even after long sputtering periods. By varying the conditions, it was found that, with a current of 50 milliamperes, a pressure of 65 microns, and anode-cathode and substrate-cathode spacings of 7-1/4 inches and 1 inch, respectively, it was possible to stabilize the discharge and to produce indium films with low resistance. The effect of sputtering time on film resistance is shown in Figure 2, in which film resistance is plotted against sputtering time. As would be expected, the film resistance was a smooth function of sputtering time, decreasing with increasing time. However, there were some irregularities as follows:

- (1) The sputtering time required for the film resistance to fall below 10 megohms (the limit of sensitivity of the meter) varied from 3 to 12 minutes for the various films. Furthermore, although resistances were checked every minute at the start of the sputtering period, the first resistance readings varied from about 500 ohms to 10 megohms.
- (2) The shapes of the resistance-time curves are not similar in all cases.
- (3) The final indium-film resistances (after 15 to 30 minutes of sputtering) varied widely.

It was apparent that sufficient control of the sputtering process had not been achieved. In subsequent studies, better reproducibility of the sputtered In films was achieved primarily as a result of better control of the gas pressure in the sputtering system and better control of the composition of the gas. Sputtering current also was adjusted to about 30 milliamperes, which helped in improving reproducibility.

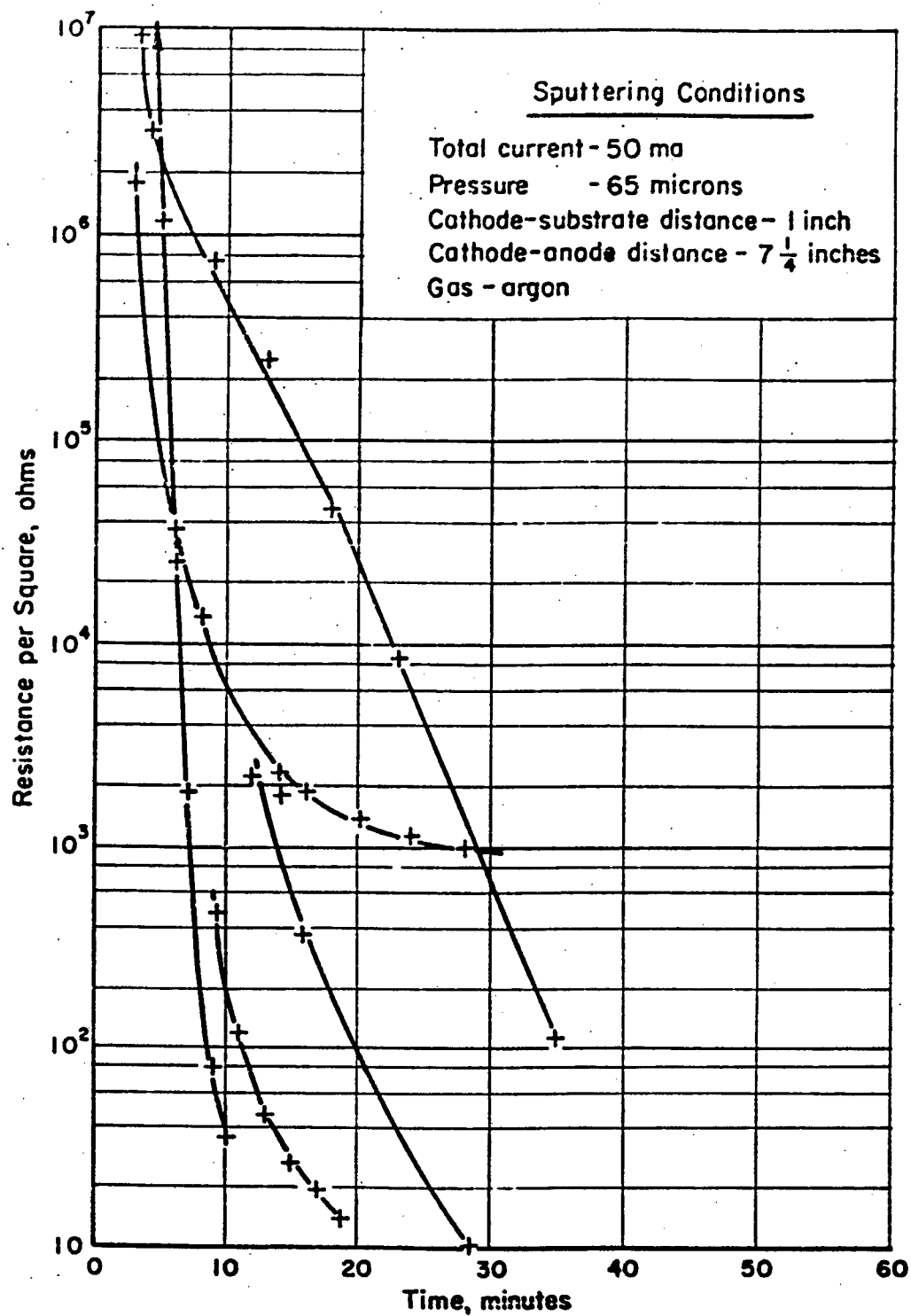


FIGURE 2. RESISTANCE PER SQUARE OF INDIUM FILMS AS A
 FUNCTION OF SPUTTERING TIME

A-11958

A thorough argon flush of the vacuum system was found to be essential to the sputtering of indium. Better control of the gas composition in the sputtering chamber was achieved by using a standardized pump-down and argon-flush schedule, and in addition, by measuring the pressure of the sputtering chamber after 10 minutes of pumping, and comparing it with previous values. The standardized pump-down and flush schedule and the measurement of the pressure in the bell jar just prior to the final filling with argon were instituted after the results of some sputtering runs indicated the importance of close control of the sputtering atmosphere. For example, in one run, it took 75 minutes to produce a 1450 ohms-per-square film, whereas the normal sputtering time for such a film is about 10 minutes. The film had a transmittance of 84 per cent, indicating that the film was oxidic rather than metallic. It was found that the ultimate pressure in the system was 14 microns, rather than the 4 microns (or less) normally expected. Apparently, enough oxygen was leaking into the system during sputtering to lower the sputtering rate, and also enough to convert the film to the oxide as it was formed.

Other factors which have been inferred by other workers to affect the reproducibility of sputtered deposits are the cathode temperature, the cathode surface condition, and the substrate temperature. Therefore, measurements of the substrate temperature were made frequently during sputtering. In addition, temperature measurements of the cathode were made under the same conditions as those used for sputtering except that there was no indium on the base plate (the cathode). No correlation between final film properties and substrate or cathode temperature could be made. In regard to the cathode condition, it has been observed when films are made with a newly formed cathode, and when films are prepared immediately after runs in which high oxygen concentrations were used, that the films are opaque and have a metallic luster instead of the usual dark-brown color, but have very low conductivity. This effect has been mentioned by others as due to "cathode conditioning", but as yet no reason for its occurrence has been found.

Conversion of Sputtered Indium Films

Three methods of converting the sputtered indium films to indium oxide were studied. Films were sputtered until their resistance attained a value between 600 and 1500 ohms per square. The films were then converted to In-O either by atmospheric-pressure oven heating, low-pressure load heating, or low-pressure oven heating. These conversion methods are discussed below.

A group of 15 films was converted in a constant-temperature oven at 244 F, and at atmospheric pressure. At the end of the first 24 hours of heating, the resistance had increased to 1000 to 2000 ohms per square and transmittance had increased from 60 to 85 per cent for some of the films. After 100 to 150 hours of heating, the films had resistance of about 10,000

to 100,000 ohms per square, and optical transmittance of 60 to 90 per cent. Resistance readings were not taken often enough during conversion to determine whether or not the resistance went through a minimum as observed with evaporated films converted at 300 F.

Seven films were converted by load heating in air at a pressure of 10 microns. Resistance of the films after conversion was about 400 to 1200 ohms per square, and light transmittance ranged from 37 to 82 per cent. However, it was difficult to obtain conversion over the entire area of the slide because of poor temperature distribution. Temperature variations exist because the geometry of the slide and film-thickness variations affect the paths of current flow in the film. The hotter portions of the film convert more rapidly. The converted portions have lower resistance; hence, the current increases through these portions and decreases in the unconverted portions of the film. Thus, as the conversion proceeds, the temperature distribution tends to become less uniform. With several films, the film-bus-bar junctions failed, and several slides cracked, because of the thermal gradients across the plate-glass slides. Because of the nonuniformity of conversion, the bus-bar failures, and the cracking of the slides, use of the load-heating method of conversion was discontinued.

Since it seemed probable that the low-pressure atmosphere was responsible for the difference in film properties between films converted by the atmospheric-pressure oven and low-pressure load-heating methods, an oven was constructed to heat the films in a low-pressure atmosphere without load heating. The construction of this low-pressure oven is described in the Experimental Details section. Six films were converted by this method at temperatures of 260 to 296 F. The resistance of all of these films went through a minimum value in several hours. The films were removed from the oven after the resistance reached the minimum. Resistance of the films was 350 to 800 ohms per square and optical transmittance was 50 to 70 per cent. The pressure in the oven was not measured.

No consistent relation has been found between the values of resistance and optical transmittance after sputtering and the ease of conversion or the values of resistance and optical transmittance after conversion. However, sputtered films that have very low resistance and are opaque and have metallic luster do not convert. Films that were converted had a resistance after sputtering ranging from 600 to 4200 ohms. These films were dark brown, with optical transmittances from less than 1 per cent to 20 per cent.

Impurity Additions to Sputtered Indium Films

From previous Battelle experience, it is known that the resistance of In-O films prepared by spraying an indium salt solution on hot glass can be reduced by addition of an antimony salt to the solution. Therefore, a study

was made of the effects of antimony doping of the films. Three methods of adding antimony were employed:

- (1) Sputtering and conversion of an indium film on an antimony oxide layer previously applied to the glass.
- (2) Overcoating of In-O films with an antimony oxide layer.
- (3) Simultaneous sputtering of indium and antimony, and subsequent conversion to the oxides.

The first two methods listed above were suggested by previous studies at Battelle (including work conducted on Contract No. AF 33(616)-342 which showed that the resistance of Sn-O films can be reduced by overcoating with antimony oxide, either by spraying or by vapor impingement.

Tin doping of In-O films by simultaneous sputtering of the two metals also was studied.

In-O Films With an Sb-O Undercoat. Glass plates, 2 x 3 inches, were coated with Sb-O as described in the "Experimental Details". Sputtering of the indium films was done in pairs, one film on a plain glass substrate, the other on a glass substrate coated with Sb-O. Sputtering conditions were: argon sputtering gas at a pressure of 100 microns, sputtering current density of about 2 milliamperes per square inch, and cathode-to-substrate distance of 1 inch.

Films were sputtered until the resistance was approximately 1000 ohms per square. They were placed in the low-pressure conversion oven at an air pressure of 50 microns and temperatures of 250 F and 300 F immediately after removal from the sputtering system. The resistance was measured as a function of time of conversion. All films showed a resistance minimum, the majority within 1 to 6 hours. Films were held at the conversion temperature until the resistance minimum had been passed and the optical transmission had leveled off.

For each pair of films, a comparison between the resistances and optical transmittances of the control films and those with Sb-O undercoats did not show any obvious improvement as a result of the Sb-O undercoating. Also, in no case are any of the undercoated films better than converted sputtered films prepared previously for other studies.

In-O Films With an Sb-O Overcoat. Initial studies of Sb-O overcoating were conducted on five In-O films prepared by sputtering-conversion for previous studies. The films had been stored in the dark (in envelopes) for some time prior to overcoating. The Sb-O coating was applied as described in the Experimental Details. A sixth film was subjected to the

same thermal treatment except that no Sb-O coating was applied. Resistance of the films ranged from 0.9 to 680 kilohms per square (dark resistance). Five of the films were heated to 210 F and subjected to SbCl₃ vapor and air, thereby depositing an Sb-O layer on the surface. The sixth film was given the same thermal treatment as the rest, but was not overcoated.

There was no appreciable change of optical transmission as a result of the SbCl₃ treatment, but the resistance of the films decreased by amounts ranging from 30 to 99 per cent, with the smaller decreases for the films of lower resistance. However, storage in the dark for 30 days caused the resistance to increase. For the films of lower resistance, the final resistance was approximately the same as before overcoating. This fact suggests that the resistance decrease brought about by the overcoating treatment was merely a result of outgassing of the films, as is believed to take place when the films are illuminated. This view is strengthened by the fact that the resistance of the control film which was only heated also decreased, and then increased to about the original value during storage in the dark.

A further study was made of Sb-O overcoating, using four converted evaporated films with minimum resistance of 250 to 350 ohms per square. The films were first exposed to light to minimize the resistance, then filmed with Sb-O, and finally exposed again to light. Minimum resistances after overcoating were all higher than those obtained before overcoating. It is clear that overcoating with Sb-O is not promising as a means of reducing the resistance of In-O films.

Antimony Doping by Simultaneous Sputtering. Glockler and Lind* and Massey and Burhop** cite references indicating that composite films may be prepared by sputtering from a cathode composed of two elements. Films have been prepared from cathodes of either intermetallic compounds or alloys. However, there are not, as yet, data or a theory to predict the composition of the film from the composition of the cathode.

An In-Sb cathode was made by melting and mixing 95 per cent indium and 5 per cent antimony, cooling the liquid to form a solid ingot, and cold-rolling the ingot into sheet form. From the physical appearance of the etched In-Sb ingot, and the phase diagram for these materials, the probable form of the ingot was InSb crystals imbedded in a polycrystalline-indium matrix. The InSb crystals were about 1 cubic millimeter in size. When this ingot was rolled, the InSb crystals were crushed. Therefore, the surface of the rolled sheet was composed of fine granules of InSb compressed in the soft indium.

*G. Glockler and S. C. Lind, Electrochemistry of Gases and Other Dielectrics, New York, J. Wiley and Sons, Inc., (1929), p. 420.

**H. S. W. Massey and E. H. S. Burhop, Electronic and Ionic Impact Phenomena, Oxford, The Clarendon Press, (1952), p. 589.

The In-Sb cathode was installed in the same way that previous cathodes were installed, that is, by pressing the ductile sheet material to the aluminum base plate, thereby making both electrical and thermal contact. The sputtering surface area, the geometry between the cathode and substrate, the slide supports, and the discharge conditions were all the same as for films sputtered from pure indium cathodes. Spectrographic analysis of two films gave antimony contents of 8 ± 1 and 10 ± 1 per cent.

Conversion at 300 F takes place more rapidly and seems to produce films with properties comparable to those produced at 250 F. Therefore, conversion at 300 F was used in these studies. In addition, to decrease further the time for processing films, the conversions were done in an atmospheric-pressure oven, where many more films can be converted simultaneously than can be converted in the low-pressure oven.

For comparable sputtering times, the resistance and optical transmission was higher for the In-Sb films than for films prepared from an indium cathode. During conversion at 300 F, the films exhibited a minimum resistance as expected. The time to reach the resistance minimum varied from 1 to 10 hours during total conversion times up to 72 hours. This compares to 30 minutes to 5 hours for In-O films. No correlation was observed between film properties and the time required to reach minimum resistance.

Figure 3 shows the data for In-Sb-O films and In-O control films. This graph shows the minimum resistance (after exposure to light) and optical transmittance of these films. It may be seen that none of the In-Sb-O films are as good as the In-O films.

Measurement of haze* on a number of the doped films gave values of 26 per cent, 14 per cent, 5 per cent, 4 per cent, and less than 1 per cent. The high-haze films have a white, powdery appearance. Undoped films generally have less than 2 per cent haze. These facts suggest that the doped films may be composed of two phases, that is, antimony oxide and indium oxide.

After conversion, the films were exposed to light to obtain the resistance minima for the films. In most cases, the resistance of the doped films decreased less than that of the undoped films.

These data show that for a nominal 10 per cent antimony in indium films prepared by sputtering, the resulting In-Sb-O films do not have a lower resistance, while retaining high optical transmission, than do In-O films. Changing the antimony concentration might result in improvement.

*Measured with apparatus conforming to Federal Specification LP-406 B, Test Method 3021.

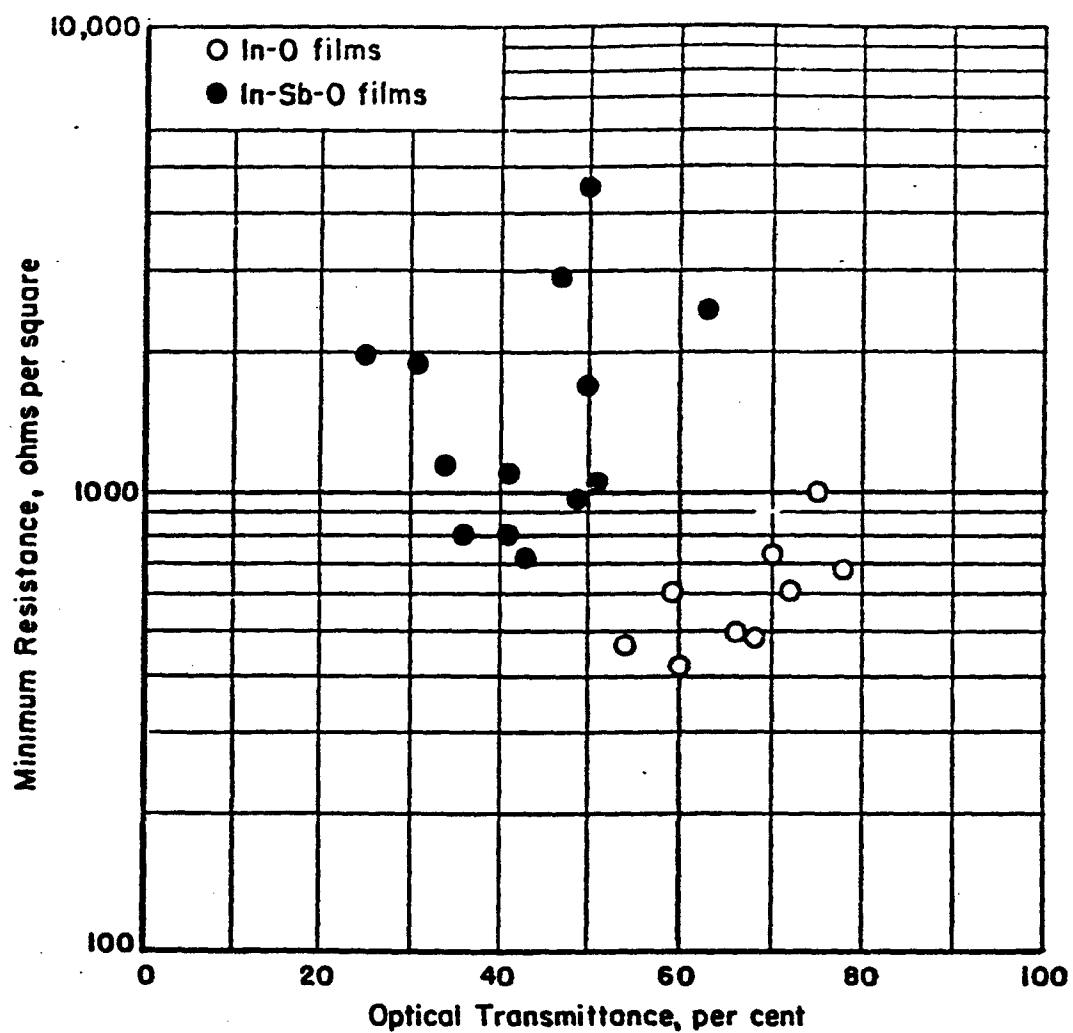


FIGURE 3. RESISTANCE AND OPTICAL TRANSMITTANCE OF UNDOPED AND ANTIMONY-DOPED In-O FILMS PRODUCED BY THE SPUTTERING-CONVERSION PROCESS

A-14302

Tin Doping by Simultaneous Sputtering. As in the case of the sputtering experiments with antimony-doped films, the cathode material used for tin doping was a sheet of alloy. An In-Sn alloy was made by mixing and melting 95 per cent indium and 5 per cent tin, casting an ingot and cold-rolling the ingot into sheet form. Unlike the In-Sb sheet, the In-Sn alloy was a solid solution.

Sputtering was carried out using the same processing parameters as in the case of In-Sb or pure indium cathodes. Spectrographic analysis of one film showed 6.5 per cent tin, based on total metal.

Nine films were sputtered from the In-Sn cathode. Their resistance ranged from 500 to 1500 ohms per square. The sputtering times of films sputtered from the In-Sn cathode are comparable to those from the undoped cathode. The tin-doped films were converted at 300 F and reached a minimum resistance during conversion. The time to reach the minimum resistance varied from 4 to 135 hours.

Normally, the conversion of In films was considered to be complete when the minimum resistance had been reached and passed and the transmission leveled off to increase less than a few per cent per day. However, the optical transmission for the tin-doped films was still increasing quite rapidly when minimum resistance was reached.

Resistance and transmittance values for In-O and In-Sn-O films are compared in Figure 4. The resistances shown are the lowest values reached during conversion (not under illumination). It will be noted that four In-Sn-O films having comparable optical transmission to that of the undoped films, had resistance values that are considerably lower than those of the undoped films. The doped films on further conversion still had lower resistance than undoped films with comparable transmission. Five other In-Sn-O films had lower resistance as well as lower optical transmission at the minimum point. However, these films, when converted further, still had lower resistance for comparable transmittance values than did the In-O films.

These data indicate that some improvement can be made in the properties of sputtered indium films by the addition of tin to the cathode material. Further improvements could be expected by finding an optimum concentration of tin in the cathode and an optimum thickness for the metal films.

The Effect of Magnesium Fluoride Antireflecting Layers on the Reflectivity of In-O Films

The intensity of the light reflected from solid materials can be reduced by the application of thin films of certain materials. The amount of reduction depends upon the respective indices of refraction and the thickness of the film material. Since one main objective of this project is to

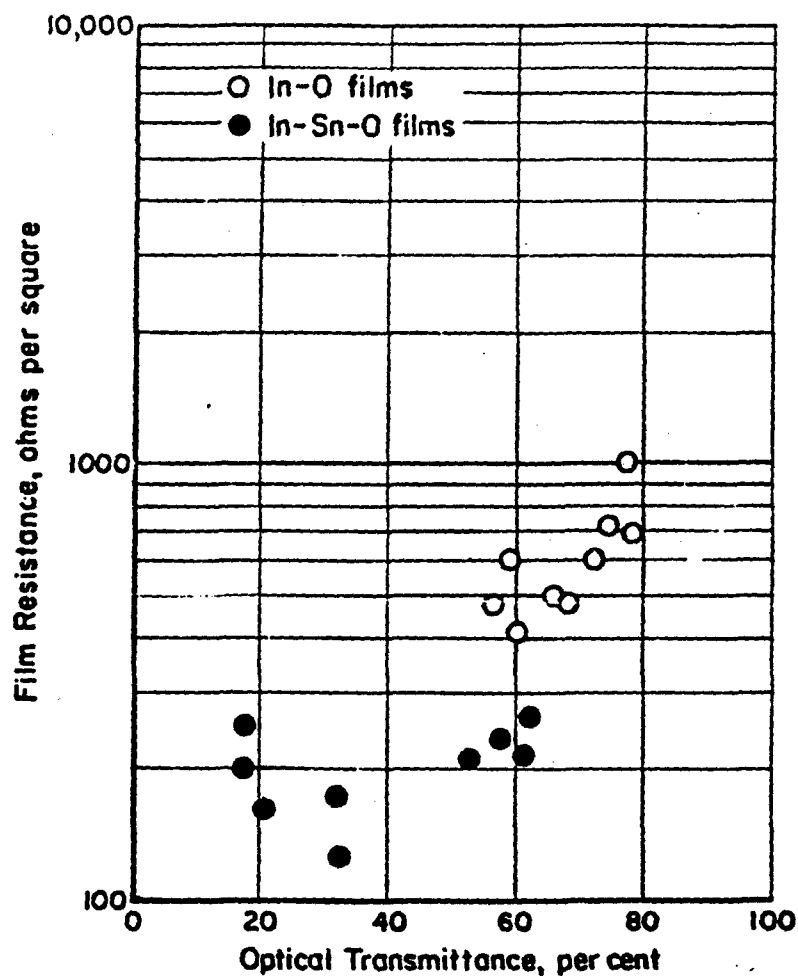


FIGURE 4. RESISTANCE AND OPTICAL TRANSMITTANCE OF UNDOPED AND TIN-DOPED FILMS PREPARED BY THE SPUTTERING-CONVERSION PROCESS

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TABLE 4. THE EFFECT OF MgF_2 COATINGS ON TRANSMITTANCE VALUES OF In-O AND In-Sn-O FILMS

Film Number	Transmittance		
	Oxide Film, per cent	Oxide Film With MgF_2 Coating, per cent	Transmittance Increase, per cent
9507-83	76	80	4
9607-86	69	72	3
9507-90	71	77-79	7
131-37A	78	82.5	4
131-49	74-77	75-80	1-3
9507-86A	74-75	79-81	5-6
131-71(1)	75	85	10
	78	84	6
	78	82	4
321-7	78-79	85-88	7-9
321-13	79	87	8
321-9B	79	87	8
131-94	75	84	9

(1) 131-71 was a film on a 3" x 4" slide; the two sets of values are for different areas of the film.

to determine the temperature coefficient of resistance and the effect of temperature cycling on the resistance.

Temperature Coefficient of Resistance

In general, T. C.* measurements showed that, although the true values were partially masked by irreversible resistance changes and the photoeffect, the approximate T. C. values were less than +0.04 per cent per degree (F). It was also found that the films of lowest resistance usually exhibit the smallest irreversible changes. Two undoped In-O films which were tested (which were also the highest in resistance) showed the greatest permanent change. Successive temperature cycles indicated a tendency for the films to stabilize, so that the resistance changes due to temperature were more nearly reversible. No adverse effects could be detected as a result of temperature cycling.

The low-temperature measurements had to be taken in a well-insulated chamber in the dark, whereas the high-temperature measurements could be taken either in the dark or in the presence of light. Films were tested under both conditions. In cases in which testing in complete darkness followed a long-time storage in the dark, the results were most nearly reversible. Typical results are shown in Figure 5 and Table 5. When the tests were continued in the dark immediately after light exposure or when both light and dark conditions were used, results such as shown in Figure 6 were obtained. In the case of the two In-O films, the permanent resistance increase during the high-temperature portion of the test was about 50 per cent. These and other results are presented in Table 6.

Environmental and Load Tests of In-Sn-O Films

Three sets of conditions were used for environmental and load testing of films: (1) continuous power dissipation of approximately 500 watts per square foot, to maintain a plate temperature of about 120 F in a stream of fast-moving air, (2) intermittent power dissipation of 1500 watts per square foot with the plate temperature controlled thermostatically at 120 F in a stream of fast-moving air, and (3) zero power dissipation in still air at an ambient temperature of 288 F. Several types of film were studied for comparison purposes: (1) sputtered In-O and In-Sn-O films, (2) evaporated In-O and In-Sn-O films, and (3) evaporated In-Sn-O films with MgF_2 antireflection coatings.

The results of the tests are given in Table 7. In none of the tests were changes observed greater than 31 per cent. Most of the films showed initial resistance increases and then gradual decreases, such that many of the films were still decreasing in resistance at the time the tests were stopped.

*This abbreviation is used for temperature coefficient of resistance.

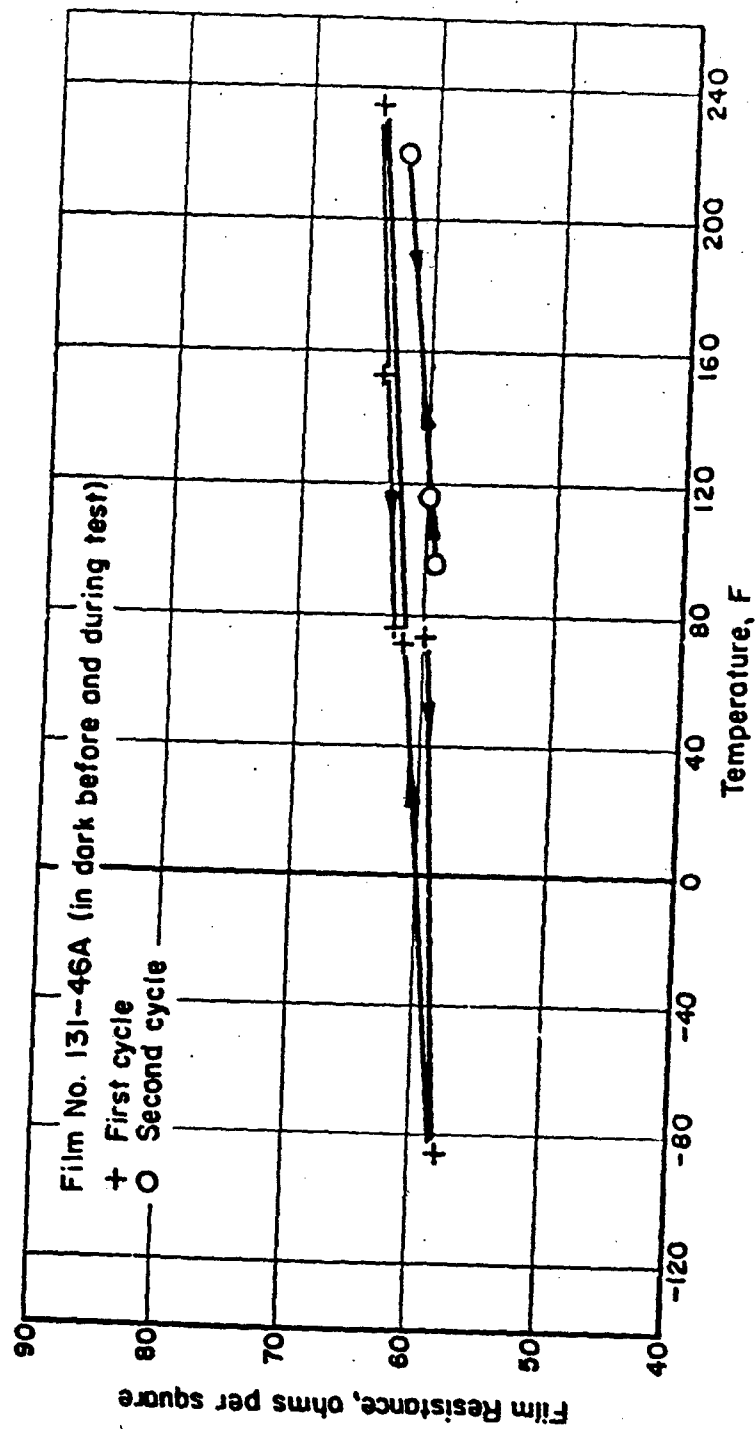


FIGURE 5. RESISTANCE-TEMPERATURE CHARACTERISTICS FOR AN EVAPORATED IN-Sn-O FILM

A-16675

TABLE 5. MEASUREMENT OF TEMPERATURE COEFFICIENT
OF RESISTANCE FOR EVAPORATED-CONVERTED
In-Sn-O FILMS UNDER TOTAL DARKNESS

Film Number	Room Temperature Resistance ⁽¹⁾ , ohms per square	Approximate T. C., per cent/deg(F)	Temperature Limits, F	Total Permanent Resistance Change, per cent
321-9A	144	+0.012	-90 to +250	6.3
321-13A ⁽²⁾	90	+0.013	-90 to +250	3.3
131-46A	60	+0.038	-90 to +230	3.3
131-13B	97	+0.010	+95 to +220	<1

(1) All measurements taken after at least 29 hours in the dark.

(2) MgF₂ coated.

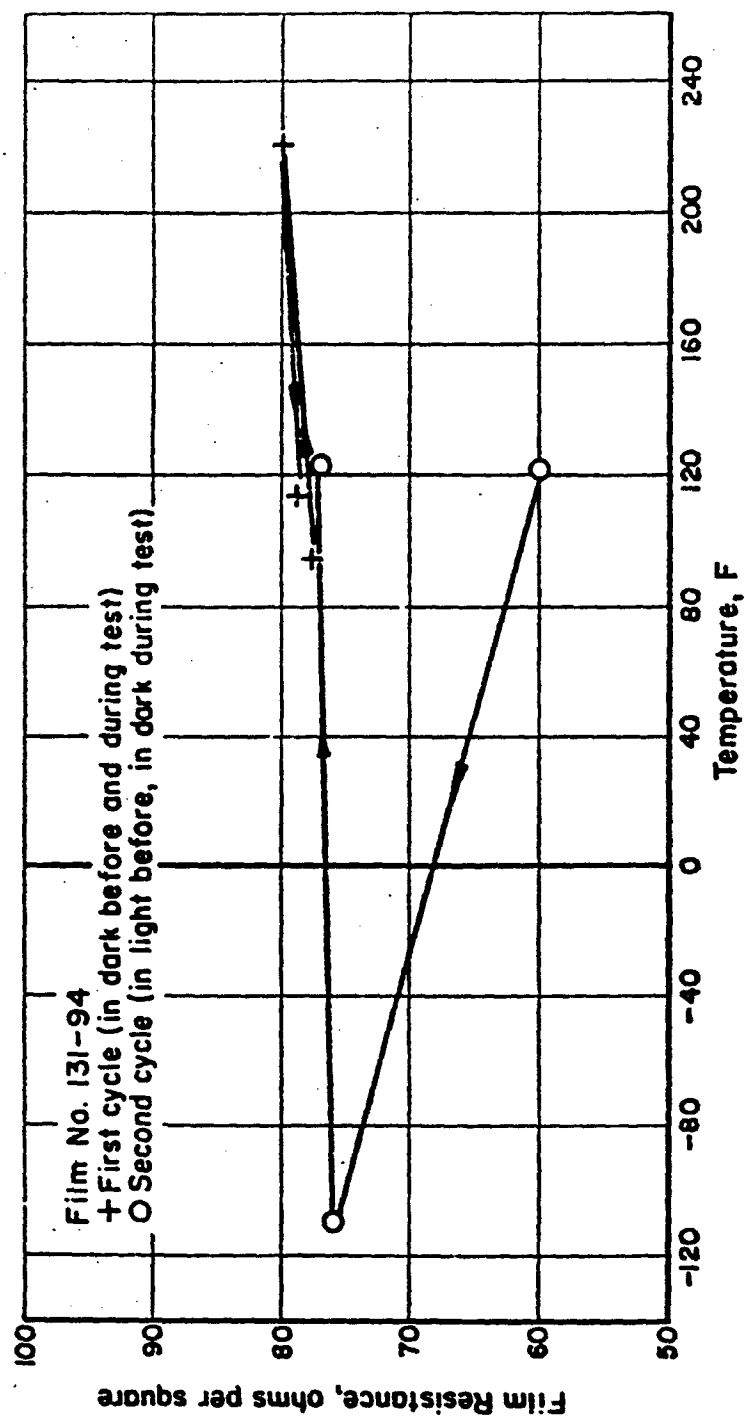


FIGURE 6. RESISTANCE-TEMPERATURE CHARACTERISTICS FOR AN EVAPORATED
 In-Sn-O FILM BEFORE AND AFTER LIGHT EXPOSURE
 A-16676

TABLE 6. IRREVERSIBLE RESISTANCE CHANGES DUE TO TEMPERATURE CYCLING
FOR EVAPORATED-CONVERTED In-O AND In-Sn-O FILMS

Film Number	Cycle	Temperature Limits, F	Initial Resistance at First Temperature, ohms per square	Irreversible Resistance Change, per cent	Light Conditions	
					Before Test	During Test
131-46A	1	+ 70 to - 90	60	3	Dark	Dark
		+ 70 to -230	62	<1	Dark	Dark
131-94	2	+120 to -120	76	32	Light	Dark
	1	+ 95 to +220	78	<1	Light	Light
	2	+ 95 to +220	78	<1	Light	Light
	3	+120 to -110	60	27	Light	Dark
321-9A	1	+ 70 to - 80	127	<1	Dark	Dark
		+ 70 to +230	127	12	Dark	Dark
	2	+ 70 to - 80	145	<1	Dark	Dark
		+ 70 to +250	147	4	Dark	Dark
321-9A	1	+ 95 to +220	245	17	Light	Light
	2	+120 to +200	287	2.4	Light	Light
	3	+120 to +220	293	<1	Light	Light
321-9B	1	+ 95 to +220	152	5.3	Light	Light
	2	+120 to +200	160	1.3	Light	Light
321-13A	1	+ 75 to - 90	90	1	Dark	Dark
	2	+ 80 to - 90	71	14	Light	Light
9507-90A(1)	1	+ 75 to - 80	155	3	Dark	Dark
		+ 75 to +250	160	50	Dark	Dark
	2	+ 75 to -110	172	11	Light	Dark
9507-95A(1)	1	+ 80 to - 80	230	1	Light	Dark
		+ 80 to +240	232	38	Dark	Dark

(1) These two films were In-O; all others are In-Sn-O.

TABLE 7. ENVIRONMENTAL TESTS OF In-O AND In-Sn-O FILMS

Film Number	Type	Test(2) Condition	Initial Resistance, ohms per square	Intermediate Resistance Changes at Various Times, per cent at hours	Final Resistance Change, per cent	Total Duration of Test, hours
9834-72	In-O, S	1	308	0 at 26	1.3	66
9834-70A	In-O, S	1	248	5 at 26	8.5	66
131-35	In-O, E	1	129	-9 at 26	-12	66
131-29A	In-Sn-O, E	1	158	1 at 26	-2.5	66
131-39	In-Sn-O, E	1	137	7 at 26	4	66
131-39A	In-Sn-O, E	1	147	7.5 at 26	4	66
10098-59	In-Sn-O, S	1	202	7 at 26	10	66
10098-63	In-Sn-O, S	1	308	1 at 26	-1	66
131-13B	In-Sn-O, E	2	94	7 at 71	4	264
321-9A	In-Sn-O, E	2	198	15 at 16	5	28
321-9B	In-Sn-O, E(3)	2	141	7 at 16	0	28
131-13A	In-Sn-O, E(3)	2	95	37 at 71	31	264
131-37	In-Sn-O, E	3	85	21 at 65	30	161
131-46A	In-Sn-O, E	3	63	-5 at 65	-1	161
131-94	In-Sn-O, E(3)	3	77	12 at 65	15	161

(1) Type: S refers to sputtered-converted films.

E refers to evaporated-converted films.

(2) Test Conditions: 1. Continuous load, 500 watts/sq ft

2. Intermittent load, 1500 watts/sq ft

3. No load, 288 F ambient

(3) With MgF₂ overcoating.

On the basis of the data obtained, there does not appear to be any correlation between stability and type of film, method of fabrication, or whether or not the film was coated with magnesium fluoride.

For the condition of continuous power dissipation, the maximum power that was supplied to the films was such that the temperature did not exceed 120 F. The blower that was used provided a stream of air sufficient to allow power dissipation of about 500 watts/sq ft without exceeding 120 F.

The average temperature of the plates tested with intermittent power dissipation was 120 F, although the temperature varied between 90 F and 140 F.

Fundamental Studies

Several In-O films were subjected to a fundamental investigation in an effort to determine the basic differences between films prepared in different ways and having different properties. The group of films studied consisted of three films prepared by evaporation-conversion, three prepared by sputtering-conversion, and three prepared by spraying a solution of InCl_3 in methanol (50 per cent by weight) on glass heated to 1150 F. The films were studied by means of X-ray and electron diffraction and electron microscopy. In addition, film thicknesses were measured by means of micro-interferometry, so that resistivities could be calculated. The results of the study are summarized briefly in Table 8, and are discussed in more detail below.

Thickness Measurements

From two to eight thickness measurements were made on each In-O film. Average values are given in Table 8. The probable error is of the order of 100 Å. Measurements were not made on the sprayed films (34-8 and 2-A-1) or on the tin-doped film (131-29).

Film thicknesses were all in the neighborhood of 1000 Å, regardless of the method of preparation, except for the double film 9507-42A*. Thus, the variations in film resistance are attributable to variations in resistivity, rather than in thickness. Resistivities ranged from 2×10^{-3} to 20×10^{-3} ohm-cm for the films studied. There is no obvious correlation with the method of film production.

*This film was about twice as thick as the others, as would be expected.

TABLE 8. FUNDAMENTAL STUDIES ON In-O FILMS

Film Number	Type(1)	Conversion Temperature, F	Optical Transmission, per cent	Reflectivity, per cent	Minimum Resistance, ohms per square	Average Thickness, angstroms	Resistivity, ohm-cm $\times 10^3$	Crystal Structure	Surface Characteristics (Electron Microscope)
								Surface Bulk	
9507-31	Evap.	250	76	17	2100	1000	20	In ₂ O ₃ (4) In ₂ O ₃	Coarse-grained, bumpy
9507-42A	Evap. (double)	250	73	10	300	1800(2)	5(3)	A(5) In ₂ O ₃ +A(5)	Fine-grained, pitted
9507-95	Evap.	400	81	13	145	1100	2	In ₂ O ₃ (4) B(5)	Fine-grained, pitted
131-29	Evap. (In-Sn-O)	300	78	--	105	--	--	In ₂ O ₃ In ₂ O ₃ (6)	--
I-119	Sput.	270	73	19	780	1000	8	In ₂ O ₃ In ₂ O ₃	Coarse-grained, bumpy
9834-58	Sput.	230	62	17	650	900	6	In ₂ O ₃ In ₂ O ₃	Fine-grained
10098-1A	Sput.	310	65	18	390	900	4	In ₂ O ₃ In ₂ O ₃	Coarse-grained, bumpy
24-6	Sprayed	--	--	--	950	--	--	In ₂ O ₃ (7) In ₂ O ₃	Coarse-grained, bumpy
2-A-1	Sprayed	--	--	--	1000	--	--	In ₂ O ₃ (7) In ₂ O ₃	Both fine and coarse areas
Unfilmed glass	--	--	92	8	--	--	--	--	--

(1) "Evap." and "Sput." designate converted evaporated and converted sputtered films, respectively. "Sprayed" designates films prepared by spraying a solution of InCl₃ on hot glass. Film 9507-42A is a double-layer film. Film 131-29 contains 10 per cent tin by weight (based on total metal).

(2) Result of only one measurement. Another measurement gave a value of 4900 angstroms. This value probably is in error.

(3) Calculated from only one thickness measurement. See Note (2).

(4) Also includes a second minor phase or a modified In₂O₃.

(5) A and B are unidentified phases.

(6) Modified. X-ray diffraction lines are broad, suggesting solid solution.

(7) With preferred orientation.

Diffraction Studies

The crystal structures determined by electron and X-ray diffraction studies are listed in Table 8 under the headings "Surface" and "Bulk", respectively. All of the films were found to contain In_2O_3 . However, there were some irregularities in the films prepared by evaporation-conversion and by spraying. Films 9507-31 and 9507-95 (evaporated) had slightly modified electron diffraction patterns. There were variations in intensity in the In_2O_3 lines and additional faint lines, suggesting the presence of a minor second phase or a modification of the In_2O_3 structure. The bulk structure of Film 9507-95 is unidentified (Phase B). The X-ray diffraction picture for this film was very poor, consisting of only faint diffuse lines. It is probable that the crystallite size was too small to give a good pattern. Film 9507-42A (double, evaporated) consisted of an unidentified material (Phase A), with In_2O_3 as a minor phase in the bulk material. The tin-doped film (131-29) had the In_2O_3 lattice, but the X-ray lines were broad (but not diffuse) suggesting that the tin was dissolved in the lattice. Another, less likely, possibility is that tin oxide was present as a second phase with very small crystallite size. The electron diffraction patterns for the two sprayed films (34-8 and 2-A-1) showed preferred orientation.

There is no obvious correlation between the film structures, as determined by X-ray and electron diffraction, and the electrical and optical properties of the films.

Electron Microscopy Studies

Electron micrographs were made of several areas of each In-O film*. Although the results of the investigation could not be correlated with film properties and production conditions, the micrographs are discussed briefly below, as a matter of record.

In general, there were two types of surface irregularity: flat bumps ranging from 500 to 5000 angstroms in diameter and fine pits 100 to 300 angstroms in diameter. The surfaces of the individual films were as follows:

Film 9507-31. Bumps 500 to 1000 Å across and about 200 to 300 Å high.

Film 9507-42A. Fine-grained background. Pits 100 to 150 Å wide, and sparsely scattered bumps 500 to 5000 Å wide and 200 to 500 Å high.

Film 9507-95. Pits about 200 Å wide. Very few bumps, about 5000 Å wide.

*The tin-doped film (131-29) was not studied.

Film I-119. Bumps 500 to 5000 Å wide and 200 to 300 Å high.

Film 9834-58. Fine grained. Grain size 250 to 500 Å, and deep boundaries 50 to 100 Å wide. A few low broad bumps up to 2500 Å wide.

Film 10098-1A. Bumps up to 2500 Å across. Boundary depressions 50 to 500 Å wide.

Film 34-8. Fine dispersion of pits 200 to 300 Å wide. Few bumps. Similar to Film 9507-42A.

Film 2-A-1. Irregular in structure, with fine-grained areas similar to 9834-58 and coarse areas similar to 9507-31 and 10098-1A.

Recommendations

In view of the promising results achieved during these studies, it is clear that additional work should be done to permit development of the films for use in aircraft.

It is recommended that research be conducted along two general lines, (1) development of techniques and apparatus for applying the films to plates of a size comparable to that used in aircraft, and (2) improvement of film properties and reproducibility of preparation. In addition, choice or development of a suitable low-reflectance coating should be made.

The application of the films to larger panels would involve considerations of uniformity and control of thickness, resistance, and optical properties. These studies should strive to attain optimum apparatus design and control of the optimum combination of processing parameters.

The improvement studies would involve considerations of additives to the In-O system, effects of varying evaporation and conversion conditions, (pressure, evaporation rate, substrate temperature, etc.) glass preparation, and other film systems if necessary. Fundamental studies and complete evaluation testing should be used where applicable in determining or improving film properties.

EXPERIMENTAL DETAILS

Materials

The sources and purities of the materials used for film deposition were as follows:

- (1) Indium: obtained from the Indium Corporation of America; reported to be 99.97+ per cent pure (the same material as has been used previously on this project).
- (2) Tin: Foil obtained from J. T. Baker Chemical Company; purity unspecified.
- (3) Antimony: commercial grade, zone refined at Battelle; spectrographic analysis shows 38 parts per million of impurities.

Dual Evaporation Source

The dual evaporation source used for simultaneous deposition of indium and tin consists of two identical sources mounted in a stainless steel clamp. A cross-sectional view of one source is shown in Figure 7. The source consists of a molybdenum rod $17/32$ inch in diameter and $1-3/8$ inches long, with a depression $3/8$ inch in diameter and $1/8$ inch deep in the top end to hold the metal being evaporated. A hole in the other end $13/32$ inch in diameter and $1-3/16$ inches deep accommodates a heating coil (about 12 inches of 0.014-inch tungsten wire). The coil is wound on a fused-silica tube, and is insulated from the molybdenum by a porcelain tube. The molybdenum rod is enclosed in another porcelain tube to insulate the source from the stainless steel clamp, and to reduce heat loss from the sides of the source. The assembly rests on a porcelain disk containing holes for the heater leads. A thermocouple well just under the indium (or tin) cavity accommodates a platinum-platinum rhodium thermocouple.

The source described above is quite efficient. The power input required for the operating temperatures used in this work (about 700 C) is of the order of 50 watts.

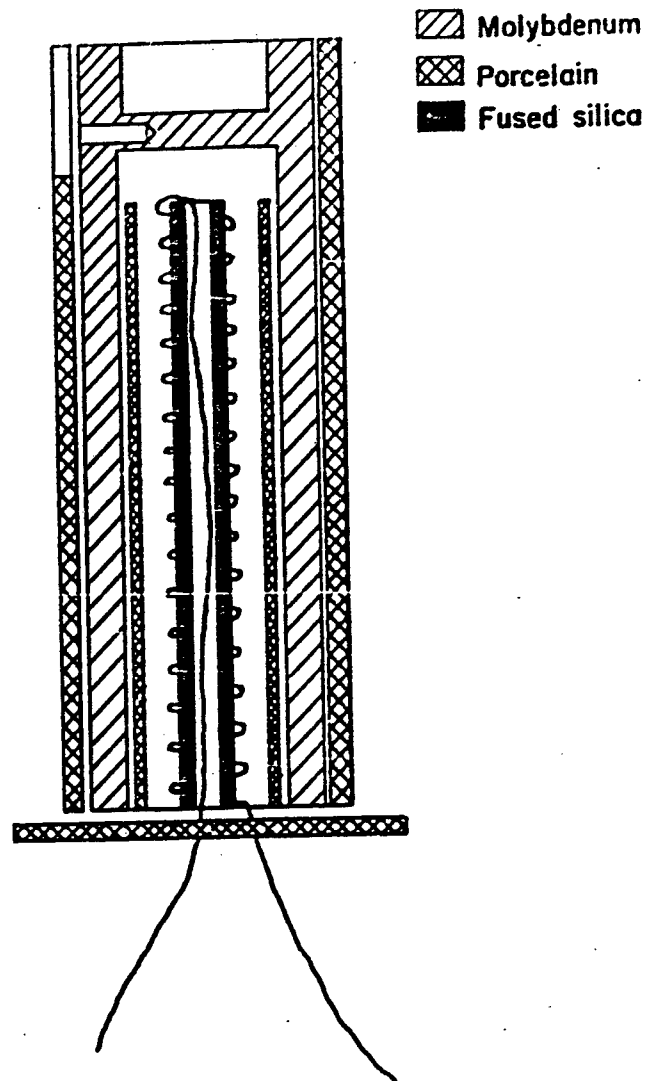


FIGURE 7. EVAPORATION SOURCE

A-14301

Oxidation Apparatus for Evaporated Films

A small oxidation furnace was constructed to permit both light-transmission and resistance measurements to be made during oxidation. The furnace consists of two concentric copper cylinders fastened between two end plates containing glass windows. The diameter of the inner cylinder is 3-1/2 inches, and of the outer cylinder 4-1/2 inches. The cylinders are 5 inches long. The furnace is heated by circulating hot oil between the two concentric cylinders. The furnace is placed in the light path of the standard optical transmission apparatus. The slide holder is fitted with leads for resistance measurements.

Resistance Stability Tests on Evaporated Films

The apparatus used for the room-temperature resistance-stability tests consists of a light-tight airtight box fitted with electrical leads to accommodate six films. The lid of the box is made of Lucite to permit illumination of the slides. A second light-tight lid is placed over the Lucite lid during the dark portion of the cycle. For part of the testing, the air in the box was dried with magnesium perchlorate. The films also were tested in humid air by placing a container of water in the box. All resistance measurements were made with a portable Wheatstone bridge. During the light portion of the test, illumination was supplied by two 15-watt fluorescent lights placed outside the box and about 2 inches above the films. Fluorescent lighting was used to minimize heating of the films during the test.

Sputtering Apparatus and Conditions

Sputtering experiments were performed in the glow-discharge and sputtering system described in WADC Technical Report 54-325. The material to be sputtered was a sheet of indium or indium alloy which formed the active surface of the cathode. The gas used in the discharge system was argon. The substrates were 1 by 3-inch glass microscope slides or 2 by 3-inch soda-lime window glass plates. To insure clean surfaces, the slides were scrubbed with detergent, rinsed in hot water, rinsed with distilled water, dried on a paper towel, and then flamed for about 10 seconds in a Bunsen burner.

In the initial studies, the anode was spaced 7 inches from the cathode. Various spacings between the cathode and the substrate were investigated. The final value chosen was one inch and was maintained by pyrex glass spacers.

Sputtering currents of 30 to 100 milliamperes were studied. The higher sputtering currents, 70 to 100 milliamperes, resulted in increased glow-discharge instability and increased frequency of bus-bar failures. Subsequently, all slides were sputtered with a current of 30 milliamperes. Use of this lower current resulted in greater discharge stability than was the case with higher current, and, in addition, eliminated bus-bar failures.

The glass supports for the slides become coated with indium during sputtering. When these supports were resting on the cathode, arcing occurred between the cathode and the indium coating on the supports, causing intense local heating of the cathode. This effect was eliminated by repositioning the supports so that they do not touch the cathode. Supports for the slide were also found to produce a shadow effect; that is, portions of the film were abnormally thin, as a result of interposition of support material between the substrate and the indium cathode. Supports were redesigned to minimize the shadowing effect.

In addition to measurements of the current and pressure, the discharge voltage, the temperature of the substrate, and the resistance of the film formed were measured at intervals during the sputtering process. Bus bars of Hanovia bright gold were painted on the substrate at each end, so that electrical connections could be made to the film. Connection was then made to an external ohmmeter through lead-throughs, and film resistances were measured during the sputtering process.

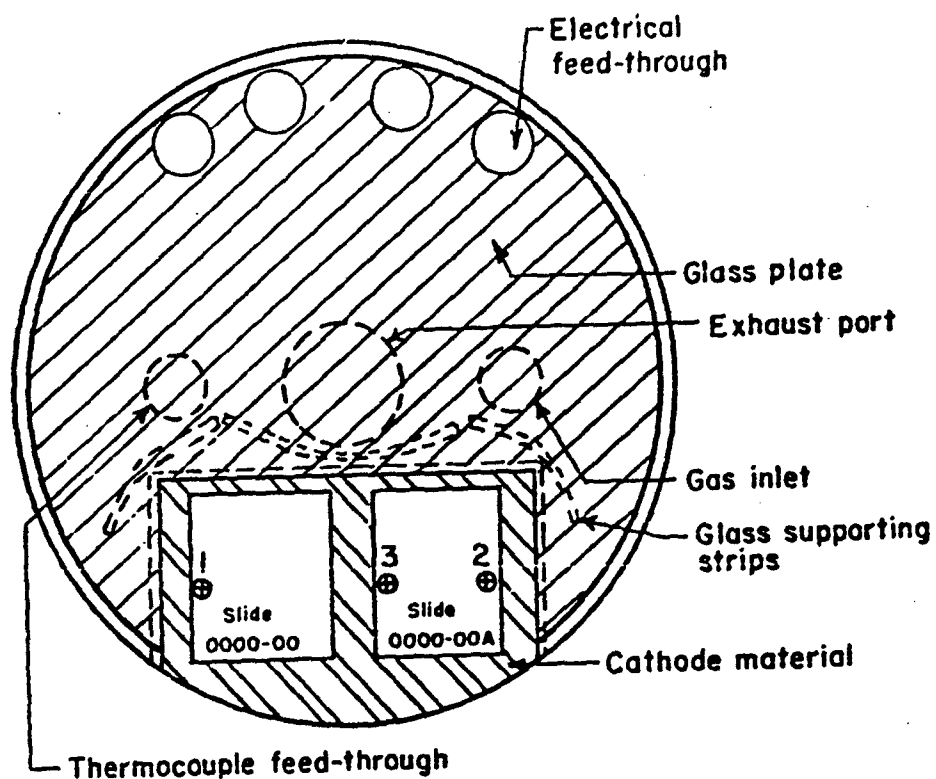
A number of sputtered slides were unsatisfactory because of bus-bar failure. The failure occurred at the junction of the film and the bus bar, causing a high-resistance strip at the junction. Evaporated-gold and evaporated-aluminum bus bars were tried, without improvement. Later, the lowering of the sputtering current alleviated the situation, as has been discussed previously.

Temperature Measurements During Sputtering

Measurements of the temperature of the substrate were made during the sputtering process. In initial attempts to measure the temperature, cold-junction temperatures within the bell jar introduced errors. Thereafter, the cold junction was kept outside the bell jar. Figure 8 shows the arrangements of the substrates in the sputtering system and the position of the thermocouples on the substrates.

Thermocouples 1 and 2 were placed in comparable positions near the outside edge of the two slides. Thermocouple 3 was located near the inside edge of one slide.

The emf of each thermocouple was measured with a multichannel strip-chart recorder. It is recommended that the strip-chart recorder be



⊕ Denotes position of thermocouple

FIGURE 8. PHYSICAL ARRANGEMENT OF SPUTTERING SYSTEM SHOWING POSITION OF THERMOCOUPLES

A-14300

grounded for best operation. However, grounding the recorder also grounded the thermocouples. As a result, the glow discharge was adversely affected because the thermocouples acted as a cathode. With the recorder not grounded, sparking occurred at the switch contacts in the recorder. The accuracy of the strip-chart recorder running at high potential above ground was checked with a portable potentiometer. The temperature difference of the substrate, as measured by both methods, was within 10 degrees F.

Table 9 lists the temperatures of the substrates for several pairs of slides. The values shown in the table are the temperatures just before the glow discharge was turned off. In most cases, temperature increased continuously during sputtering, but in a few cases, the temperature reached a maximum and then decreased.

Temperature measurements of the cathode were made, along with other temperature measurements, using the strip-chart recorder. These measurements made during the actual sputtering of the film with the thermocouple protected indicated that the temperature of the cathode varied from 50 F to 125 F from one sputtering run to another. Eighteen of the readings out of 24 selected were between 70 F and 90 F. There was one cathode temperature reading of 195 F. It is possible that the thermocouple was not making good thermal contact with the cathode when this previous measurement was made. Since the gas temperature is higher than the cathode temperature, poor contact would cause the measured temperature to be too high.

Thermal Conversion of Sputtered Films

Load heating was done in the sputtering system. After the film was sputtered, the bell jar was pumped down, then air was admitted until the pressure reached 10 microns. Temperature and resistance measurements and visual observations were made at intervals while load heating.

The low-pressure oven consists of a small ceramic plate heater mounted in a vacuum desiccator. The slides were placed on an aluminum sheet which touched the heater. A mechanical oil pump was used to evacuate the desiccator. Pressure in the low-pressure oven was not measured. The temperature of the slide was controlled by varying the input power to the heater. Leads also were brought out of the oven to measure the resistance of the film. The oven was evacuated for 15 minutes after the films were put in the oven and before the heat was turned on.

Application of Sb-O Undercoating and Overcoating

To form an Sb-O undercoat, glass plates to which gold bus-bars had previously been applied were heated in an oven to temperatures from 200 F

TABLE 9. TEMPERATURE OF SUBSTRATE DURING SPUTTERING

Slides sputtered at 100 μ , 30 ma

Sputtering Time, minutes	Temperature of Substrate During Sputtering, F				
	Slide A, Right Side	Unlettered Slide, Left Side	Thermocouple 2 Minus	Slide A, Left Side	Thermocouple 3 Minus
	(Thermocouple 1)	(Thermocouple 2)	Thermocouple 1	(Thermocouple 3)	Thermocouple 1
2.5	105	128	21	140	35
3.5	115	136	21	149	34
3.5	119	141	22	153	32
5	122	135	13	96	-26
5	124	135	11	107	-17
5	125	135	10	109	-16
5	126	148	16	113	-13
5	129	171	42	180	51
5	130	144	14	96	-34
5	130	182	52	190	60
5	134 ^(a)	147	13	--	--
5	137	210	73	--	--
5	150	200	50	--	--
5	163	194	31	--	--
5	175 ^(b)	177	2	--	--
7	158 ^(a)	160	2	--	--
10	135	163	28	114	-21
10	144	161	17	133	-11
12	110	140	30	--	--
12	129	159	30	--	--
12	155	168	13	--	--
30	165	220	55	241	67
30	176	220 (222)	44	216	40

(a) Measured with portable potentiometer only.

(b) Temperature readings somewhat erratic.

to 1150 F. The bus bars had previously been coated with a protective paint. The heated plates were either sprayed with an HCl solution of SbCl_5 or subjected to SbCl_5 solution. The spraying was done in short bursts, with reheating of the glass between bursts.

Overcoatings were applied in a somewhat similar manner except that the indium oxide-coated plates were heated only to 210 F. After a 2-minute heating period, the vapors of SbCl_3 were impinged on the films until a change in reflected color was observed.

Application of Magnesium Fluoride Overcoating to In-O Films

The deposition of MgF_2 on In-O films was carried out in a bell jar vacuum system. The In-O films and evaporation source were separated by a distance of 6-1/2 inches. The evaporation source was constructed of 0.010 inch molybdenum sheet. An incandescent tungsten lamp was installed in the vacuum system with a piece of frosted glass for a light diffuser. The deposition of magnesium fluoride was observed in a mirror on the film, on a clear glass monitor strip, and on a tantalum metal monitor strip.

In-O films were cleaned by brushing with an antistatic brush. The film was placed in the holder in the vacuum system and approximately 100 milligrams of powdered c. p. MgF_2 was placed in the evaporation boat. Thermocouples were placed in the holder in contact with the In-O film and the evaporation boat. A rotating metal shield was placed between the source and film. The vacuum system was then evacuated to a pressure of 1 to 2×10^{-5} mm Hg. The MgF_2 was heated at temperatures up to 900 C until the pressure again returned to 1 to 2×10^{-5} mm Hg. After this outgassing, the temperature of the source was raised until the deposition of MgF_2 was observed to take place on the source side of the metal shutter. This occurred at about 1100 C. When the desired amount of MgF_2 had been deposited upon the In-O film, as estimated from the color, the shutter was interposed between the source and film and the source power was reduced. During this operation, the film temperature did not rise above 150 F. The time for the deposition of the magnesium fluoride layer was about 1 to 2 minutes. After allowing a short time for the cooling of the evaporation boat, air was allowed to enter the system and the MgF_2 -coated In-O film removed.

On several of the first slides coated, resistance values were measured before and after coating. Only small changes in film resistance took place. The optical transmission data were taken before overcoating and after overcoating in comparable areas of the film.

Measurement of Temperature Coefficient of Resistance

Low-temperature resistance measurements were made in a double-wall chamber, the outside of which was insulated with cork. A mixture of dry ice and acetone was placed between the walls of the chamber. The films were suspended in the inner chamber by electrical leads which passed through the insulated cover, and to which external connections were made for the resistance measurements. Because of the confined space in the chamber, it was necessary to conduct all of the low temperature tests in total darkness.

For the measurements at high temperature, a larger unit was used which permitted the use of an internal light to illuminate the films.

Electrical Load Tests

Load tests were conducted simultaneously on four films with individually controlled power supplies. The films were mounted perpendicular to the air flow from a blower. Fenwall thermostats Type 32000-1 were mounted on the film surfaces, with a thin sheet of mica insulating the thermostats from the films.

In the continuous load tests, current, voltage, and temperature were monitored on a multichannel recorder.

(Data for this report are recorded in Battelle Laboratory Record Books Nos. 8923, pages 1-100; 9507, pages 1-100; 9657, pages 1-100; 9834, pages 1-100; 10070, pages 1-100; 10098, pages 1-100; 10131, pages 1-100; 10185, pages 1-100; 10097, pages 1-55; 10321, pages 1-42; and 10341, pages 1-33.)

PS:EHL:LHM:REB:EHL:ERO:HLG/pt

APPENDIX

LITERATURE SURVEY, BIBLIOGRAPHY, AND REVIEW OF INVESTIGATIONS AT BATTELLE AND BALCO

Literature Survey

A review of the technical literature has been made for the purpose of obtaining information pertinent to production of transparent conducting coatings, as required by Exhibit A of the contract. The survey was not intended to be a comprehensive study of all the published information concerning production and properties of films in general, although it is conceded that such a survey could be valuable. The large number of writings on some phases of this broad topic, for example, evaporation and sputtering of metals, would make the cost of such an undertaking prohibitive. Therefore, the survey was limited, primarily, to studies of transparent conducting films, and those investigations of metal films which are particularly pertinent to the work on transparent conducting coatings now in progress at Battelle and elsewhere. Studies which are principally of historical interest are not included.

The following review consists of two parts. The first section is a discussion of patents. The second section describes research investigations reported in other technical literature.

Patents

Transparent conducting films of stannic oxide may be formed by applying a tin compound, such as SnCl_2 or SnCl_4 to hot glass (1, 6, 10, 15, 17, 18, 30). The glass must be maintained at a high temperature (about 500 to 700 C) during application. Application is made by spraying or dipping the glass, or by flowing vapor over it.

For dipping or spraying, the tin salt may be used as an aqueous (10, 17) or alcoholic (15, 17, 30) solution. Addition of alcohol to aqueous solutions has been claimed to reduce haze in the films. (15) It has also been stated that, with aqueous solutions, too low a concentration of tin salt causes haze, whereas too high a concentration causes the film conductivity to be low. (17) For application of the tin compound to the glass as a vapor, it has been claimed that mixing the vapor with CO_2 reduces haze in the films. (17) Another method of vapor application consists of joining two streams of air at the glass surface, one stream containing SnCl_4 and the other containing water vapor. (10) This procedure permits most of the hydrolysis reaction to take place in the vicinity of the glass.

Other inorganic tin compounds⁽¹⁰⁾ which have been used for production of tin films by the above methods are SnI_2 , SnSO_4 , $\text{Sn}(\text{SO}_4)_2$, and $\text{Sn}(\text{NO}_3)_2$. Several organic tin compounds also have been used.⁽⁷⁾ An example is dibutyl tin acetate, used both alone and in organic solvents. It is claimed that use of the organic compounds reduces haze, which, according to the author of the patent, is caused, partially, by the HCl liberated when tin chlorides are used. Films also have been formed by applying solid stannous oxide and solid stannous oxalate to heated glass.

Various additives have been used to improve the properties of stannic oxide films formed from tin chlorides. Metallic additives usually are applied as chlorides. Addition of a small amount of antimony^(5, 18, 19, 20) lowers the resistance of the film; too much antimony raises the resistance. The minimum resistance (reported to be about one-twentieth of that of a pure SnO_2 film) is obtained with an antimony concentration of about 1 per cent.⁽¹⁹⁾ Antimony also is said to stabilize the resistance of the film.⁽²⁰⁾ Additions of reducing agents, for example, phenylhydrazine⁽¹¹⁾, and of fluorides, e.g., $\text{NH}_4\text{F} \cdot \text{HF}$ and NH_4F ⁽¹⁶⁾, also are claimed to reduce film resistance. Additions of chromium, aluminum, vanadium, iron, copper, zinc, manganese, cobalt, and nickel are reported to increase the resistance of SnO_2 films.^(19, 31)

Excessive haze results when SnO_2 films are applied to lime-soda glass. The haze is thought to be caused by the alkali metals in the glass. Certain additives, namely, hydrazine⁽¹²⁾, alcohols^(12, 16), aldehydes⁽¹⁶⁾, and fluorides⁽¹⁶⁾, are claimed to reduce the haze. Another method of reducing haze with lime-soda glass consists of treatment of the glass, before filming, with acid, to reduce the soda content of the surface.⁽²⁵⁾ Still another method is to deposit an intermediate film containing no alkali metals. The SnO_2 film is then deposited on the intermediate layer. Materials which have been used for this layer are oxides of copper, aluminum, lead, zinc, iron, nickel, cobalt, thallium, silver, titanium, antimony, and silicon.^(13, 25, 28)

Secondary high-resistance coatings have been employed to protect transparent conducting films from the atmosphere. The secondary films are composed of mixed tin-antimony oxides (with high antimony content). These protective films also are said to stabilize the resistance of the conducting films.⁽⁵⁾

Transparent conducting films also have been made of oxides of indium^(21, 24, 32) and cadmium^(21, 27), of mixtures of oxides of indium and tin^(5, 21, 22), and of mixtures of oxides of cadmium and indium.^(5, 23) These films are formed by the same methods as are the SnO_2 films, usually by spraying the chlorides on heated glass (500 C or above). The mixed-oxide films are claimed to have lower resistances than the films of single oxides. In the case of cadmium oxide films formed by spraying, addition of a strong oxidizing agent such as hydrogen peroxide also is claimed to reduce film resistance.⁽²⁷⁾

Transparent conducting films also have been made by applying FeCl_3 to heated glass (about 500 C) by the usual methods. These films must be cooled in a reducing atmosphere (e.g., a yellow flame) to give good conductivity. (1, 10) Other conducting films have been made with silicon tetrachloride and with salts of tungsten and molybdenum. These films also must be cooled in a reducing atmosphere. (8, 10) The patents do not state whether or not these films are transparent.

Transparent conducting films also have been made by evaporation and sputtering of platinum and gold. (9)

Films of various metals have been converted to oxide films by means of a glow discharge. (2, 3, 4) Transparency and conductivity are not mentioned in the patents.

It is difficult to make good electrical contact between the conducting films and the bus bars which are used to apply potentials across them. Poor contact causes burnouts at the film-bus bar junctions. One method which has been proposed to prevent burnouts is to make the conducting film thicker or of lower resistivity (by using additives) in the vicinity of the junction. (26) Other methods make use of special bus bars. One type consists of a layer of silver covered by a layer of platinum. The metals are fired on the base. The conducting film is then deposited so that it overlaps the platinum. This type of bus bar is claimed to make better contact than silver alone. (29) Another type of bus bar consists of a mixture of silver powder with a vitrifying enamel which is fired on the base. The conducting film is then applied. (15) A third type involves the use of a vitrifying enamel containing granular particles (e.g., Al_2O_3) to make a rough surface. This layer is applied first and baked on. The transparent film is then applied, and any type of conducting bus-bar material (e.g., air-dry silver paint) is applied as the final layer. The rough surface is said to cause good contact to be made. (14)

Other Technical Literature

Aitchison (33) studied the electrical properties of SnO_2 films prepared by spraying solutions of SnCl_2 in acetic acid and ethyl alcohol on Pyrex glass at 500 to 800 C. He found that the temperature coefficient of resistance is negative, indicating semiconductivity. Measurements of the Hall constant and thermoelectric power showed the films to be n-type. Addition of indium increased the resistance, whereas, antimony decreased it. The effects of these additives are as expected from modern views on controlled valency, since indium in a +3 state could trap an electron and antimony in a +5 state could supply an electron to the lattice. Aitchison also studied the effects of various substrates. He produced adherent, uniform films on lead glass, Pyrex (borosilicate) glass, fused silica, sapphire, periclase (MgO), and crystalline quartz. Films on NaCl , LiCl ,

stainless steel, and nickel were patchy and hazy in appearance. The effects of the substrates on electrical properties were not studied.

Fischer⁽⁴¹⁾ studied the electrical and optical properties of films of tin oxide and indium oxide prepared by spraying aqueous solutions of the chlorides on hot glass. The application temperature was not stated, but was implied to be about 700 C. He showed that addition of antimony to tin oxide films decreases the film resistivity, whereas indium and aluminum increase the resistivity, in agreement with previous workers. From measurements of Hall constant, resistivity, and optical absorption edge, Fischer calculated the following properties for the films:

<u>Composition(a)</u>	<u>Electron Concentration, cm⁻³</u>	<u>Mobility, cm²/volt-second</u>	<u>Gap Width, ev</u>
SnO ₂	1 x 10 ²⁰	6	4.1
SnO ₂ + 1.5% Sb ₂ O ₃	1 x 10 ²¹	20	4.1
In ₂ O ₃ + 1.5% CdO	3 x 10 ¹⁹	6	5.1

(a) The compositions given are the assumed film compositions, based on the proportions of materials in the spraying solutions used to make the films.

Lyon and Geballe⁽⁴⁵⁾ measured the resistance of commercial (Corning) SnO₂ films on glass as a function of temperature. They found the temperature coefficient of resistance to be negative, in agreement with the work of Aitchison.⁽³³⁾ They showed that the resistance can be represented by an expression of the form $R = aT^n$ over the temperature range 77 to 297 K. In the above expression, T is the absolute temperature and a and n are constants which vary from specimen to specimen.

Szawlewicz⁽⁴⁹⁾ studied the structure of commercial SnO₂ films by means of electron microscopy and electron diffraction. He found that the films consisted of very small tetragonal crystals of SnO₂. In films which had good conductivity, the crystals were preferentially oriented. Films which had high haze values were found to contain large holes, suggesting that additives had been used in the preparation of the films. When films were subjected to electrical overload, recrystallization occurred. The recrystallization continued along current-carrying paths, resulting in eventual film breakdown. Szawlewicz also studied an experimental SnO₂ coating formed by spin coating a solution of SnCl₄ and subsequently baking at 350 C. The film resistance was 3 megohms per square, and the adherence was poor. The coating was found to consist of extremely small, randomly

oriented crystals. The high resistance was attributed, at least in part, to the lack of orientation.

Bauer⁽³⁷⁾ studied the electrical properties of tin oxide films on quartz. The films were formed by vacuum evaporation of the metal and subsequent oxidation in air at temperatures of 300 to 800 C. Hall measurements showed that the films were *n*-type. Conductivities for the various specimens ranged from 1.4×10^{-4} to $6.6 \text{ ohm}^{-1} \text{ cm}^{-1}$. Heating in vacuum increased the conductivity. The maximum value attained on heating was $34 \text{ ohm}^{-1} \text{ cm}^{-1}$. A plot of the logarithm of the conductivity against the reciprocal of the absolute temperature gave an activation energy of a few hundredths of an electron volt, increasing with temperature. The average value of thermoelectric power was about 200 microvolts per degree C.

Bauer⁽³⁷⁾ also studied the properties of films (0.1 to 10 microns thick) of the oxides of thallium and cadmium, prepared by evaporating the metals on quartz and subsequently oxidizing in air.

The thallium films oxidized slowly in air at room temperature. After a few weeks the films were dull white. These films had low conductivity (less than $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$). Thallium films oxidized in air at 200 to 250 C were brown to yellow-red and transparent. They were believed to be a mixture of Tl_2O and Tl_2O_3 . Conductivities of these films were from 10 to 5000 $\text{ohm}^{-1} \text{ cm}^{-1}$. The temperature coefficient of resistivity was positive. Hall constants of individual specimens ranged from -0.0065 to -0.02 $\text{cm}^3/\text{coulomb}$, independent of temperature over the range -180 to +20 C. Films oxidized at 290 C were dark red and transparent. They were adherent and not easily scratched. Conductivities of these films were from 3400 to 11,000 $\text{ohm}^{-1} \text{ cm}^{-1}$. The temperature coefficient of resistivity was positive. Hall constants ranged from -0.006 to -0.013, independent of temperature (-183 to +20 C). These films became colorless when heated in air. The colorless films had low conductivities (less than $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$).

The cadmium films studied by Bauer were oxidized in air at temperatures of 300 C and higher. Oxide films greater than 3 microns thick were blue-black. Thinner films were clear and dark red. Conductivities of the films varied from 0.01 to 0.03 $\text{ohm}^{-1} \text{ cm}^{-1}$. Hall constants ranged from -0.2 to -0.8 $\text{cm}^3/\text{coulomb}$, independent of temperature. Heating the films for several hours in oxygen caused the conductivity to decrease by about 20 per cent. The temperature coefficients of resistance of high-conductivity specimens were negative, while those for low-conductivity films were positive.

The properties of sputtered cadmium oxide films were investigated by Preston⁽⁴⁷⁾ and by Helwig⁽⁴³⁾.

Preston prepared cadmium oxide films by sputtering from a cadmium cathode in air and in argon. Hall measurements showed the films to be *n*-type. Electron diffraction studies showed that the films were CdO with preferred orientation of crystallites. Films sputtered in air had much lower conductivities than did the ones sputtered in argon. When argon was used, if the apparatus was first thoroughly outgassed by pumping, or if a trace of a reducing vapor such as benzene was added to the argon, metallic cadmium films were formed.

Helwig prepared CdO films by sputtering from a cadmium cathode in nitrogen-oxygen and argon-oxygen mixtures. He found that the films were deposited more rapidly in A-O₂ mixtures than in N₂-O₂ (of the same oxygen concentration) for a given power input, but that the films formed in N₂-O₂ mixtures had higher conductivity. This fact is not necessarily in contradiction to Preston's finding that films formed in air had lower conductivities than those formed in argon, since Preston did not use the same oxygen concentration in both cases. Helwig also found that the conductivity of the films increased with decreasing oxygen pressure during sputtering for oxygen concentrations less than about 10 or 15 per cent. Electron-diffraction studies showed that films sputtered in argon containing 1 per cent oxygen had the same lattice constant as the bulk material, whereas films formed in "almost pure nitrogen" had a slightly greater lattice constant. These facts indicate that nitrogen dissolves in the lattice, but that argon does not. Further evidence for dissolved nitrogen was given by the fact that after the films (prepared in N₂-O₂) were heated to 400 C, the lattice constant was the same as that of bulk CdO. Films formed in pure oxygen had the lattice constant of the bulk material if sputtered with high power input, but if the films were formed with low power input the lattice constant was slightly greater, and there was evidence of lattice distortion (line broadening). In general, for a given sputtering gas, higher power inputs gave films of higher conductivity. Helwig suggested that this may have been the result of higher substrate temperatures at the higher power inputs.

The properties of transparent sputtered-gold films were studied by Preston and others. (34, 35, 36, 42) They found that the substrate has a great effect on the properties of the films. With glass substrates, even the method of cleaning the glass is important. Films deposited on chemically cleaned glass are blue and have high optical absorption and high resistance, whereas, if the glass is cleaned with precipitated chalk, the films are straw colored and have low optical absorption and resistance. Further lowering of the resistance may be accomplished by first sputtering a film of bismuth oxide or lead oxide on the glass and then applying the gold. If the composite films thus formed are heated to 200 C, the resistance and optical absorption are decreased still further. Films with a resistance of 10 ohms per square and optical transmission (white light) of 75 per cent were prepared by this method. It was found that use of sputtered zinc oxide as a substrate for the gold results in blue films with high resistance.

Cosslett⁽⁴⁰⁾ studied the properties of indium metal films evaporated on cellulose substrates at liquid-air temperature. He found that the films have the same structure as the bulk metal (tetragonal), but with lattice constants 0.7 per cent greater. When raised to room temperature, films produced at very low evaporation rates undergo a transition to a cubic structure. Films produced at higher rates do not make this transition. The cubic material oxidizes more easily than the tetragonal, as might be expected since the oxide is cubic. The lower the evaporation pressure (in the range 10^{-5} to 10^{-3} mm of Hg) the lower is the resistance of the resulting films. If, after deposition at 10^{-5} mm of Hg, the pressure is raised to atmospheric, the resistance increases by as much as an order of magnitude. This effect appears to be a result, at least in part, of oxidation, since the effect is greater in oxygen than in air. However, there is a similar, but lesser, effect in nitrogen, indicating that sorption also plays a part in increasing the resistance.

Clegg⁽³⁹⁾ investigated the optical properties of evaporated films of silver, gold, tin, and indium. In the case of silver (the only metal studied extensively), higher substrate temperatures during evaporation permit greater film thicknesses to be attained before the optical properties approach those of the bulk metal. In tin and indium films, the "nonmetallic" properties extend to much greater thicknesses than is the case with silver.

Suhrmann and Schnackenberg⁽⁴⁸⁾ found that metal films (Ni, Fe, Cu, Ag, Au, Pb, and Bi) evaporated at low temperatures (77.5 and 182.5 K) consist of very small crystallites. As the temperature is raised, the crystallites increase in size. This finding is similar to that of Picard and Duffendack⁽⁴⁶⁾, who found that films of zinc and cadmium evaporated at liquid-air temperature on collodion consist of smaller crystallites and have smaller interstitial distances between crystallites than do films prepared at room temperature. However, they did not find this effect with films of Al, Cu, Au, and Mg.

Levinstein⁽⁴⁴⁾ prepared films of 35 metals by evaporation, and studied their structure by means of electron diffraction and electron microscopy. He showed that with zinc and cadmium, films cannot be formed at extremely low evaporation rates, presumably because the vapor pressures of the metals are so high that they re-evaporate as rapidly as they are deposited. Uniform films can be formed at high evaporation rates. At intermediate rates, isolated crystals form on the substrate. With antimony, slow evaporation gives an amorphous film, whereas the film formed at higher rates is crystalline. The evaporation pressure also was found to affect film properties. Some metal films show preferred orientation when formed at very low pressures, but no orientation when prepared at 0.1 mm of Hg. Levinstein evaporated zinc and gold simultaneously, with the zinc evaporation rate so low that zinc films would not normally form. However, the film obtained by simultaneous deposition was shown to be a compound of zinc and gold.

Beeching⁽³⁸⁾ found that aluminum, chromium, and copper films evaporated at low rates have a more diffuse electron-diffraction pattern than films formed at higher rates. This probably indicates that the slowly formed films consist of smaller crystallites. Beeching also determined that, for aluminum, the direction from which the atoms strike the substrate affects the degree of preferred orientation of the crystallites.

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Review of Investigations at Battelle and Balco

The following section is a review of the progress reports on Contracts AF 33(616)-342 (Battelle) and AF 33(616)-111 (Balco Research Laboratories), as required by Exhibit A of the contract for the present project.

The goal of the Balco project was to produce a transparent, conducting film for acrylic plastic with a resistance of 100 ohms per square or less, and with certain optical and mechanical properties. Battelle had two goals, namely, development of (1) a film for laminated safety glass with a resistance of 100 ohms per square or less, and (2) a film for laminated safety glass with a resistance of 1 to 10 megohms per square. The

films were to have certain optical and mechanical properties, and were to be applied at a temperature of 250 F or lower, to avoid bubbling the plastic laminate.

Deposition of Films From Solution

Investigations on deposition of films from solution were conducted along considerably different lines at Battelle and Balco. In some respects, the two investigations are complementary, and, together, they form a clear picture of the capabilities and limitations of wet-chemical techniques for the deposition of transparent conducting films at low temperatures. Although none of these techniques offers much promise as a means of forming low-resistance films (100 ohms per square) with suitable optical properties, some of the methods employed were shown to be promising for production of the required high-resistance coatings (1 to 10 megohms per square). The economy and simplicity of the wet-chemical techniques makes them particularly attractive.

Work at Balco was concentrated on development of solutions and curing methods. Spin coating at room temperature, with subsequent baking at 350 C (598 F), was used for most of the work. On the other hand, much of the Battelle investigation consisted of a study of various techniques for applying the films at lower temperatures (250 to 450 F). The methods which were studied at Battelle were dipping, vapor impingement, precipitation from homogeneous solution, spraying, deposition of metal films from solution for subsequent conversion to the oxide (attempted only with cadmium), and wet-chemical conversion of evaporated metal films.

The Battelle investigation showed that, of the techniques studied, vapor impingement and dipping are the most promising methods of forming the high-resistance films at low temperatures. The vapor-impingement method permits the use of a temperature gradient through the glass, so that the surface being filmed can be maintained at a higher temperature than the bubbling temperature of the plastic laminate. The gradient is established by heating only the surface being filmed. At 250 F vapor impingement appears to be the preferred technique, whereas dipping is superior at somewhat higher temperatures (300 to 350 F). It was found that, with the dipping technique, preheating the glass before dipping causes the resultant films to have better conductivity. However, even with preheated glass, the specimens also must be baked after application of the film, to attain maximum transparency and conductivity.

The other application techniques named above show little promise for preparation of satisfactory films at low temperatures. Spraying gives non-adherent, powdery films. Films prepared by precipitation from homogeneous solution are hazy and nonconducting. Wet-chemical conversion of

metal films gives extremely hazy films or removes the films from the substrates. The attempts to deposit metallic cadmium resulted in either white, nonadherent deposits or no deposits.

Balco studied the use of various wetting agents and thickeners to improve the uniformity and increase the thickness per coat of solution-deposited films. The best wetting agent and thickener which they studied were Aerosol OT and carboxymethyl-hydroxyethyl cellulose (CMHEC), respectively. Since Balco's goal was the development of only a low-resistance film, they used multiple coating, and, in most cases, the properties of the films after only one or two coats are not reported. However, in view of their success with wetting agents and thickeners in forming low-resistance films, it seems likely that these materials might also be useful in the preparation of high-resistance coatings, using only single coats.

At Battelle, most of the solution-deposition investigation was done with chlorides of tin and titanium. Little work was done with cadmium or with other compounds of tin and titanium. Transparent conducting films (a few megohms per square) were formed by dipping preheated glass in solutions of SnCl_4 and TiCl_4 , and by impingement of SnCl_4 vapor. Balco, on the other hand, studied deposition of films from solutions of various compounds of tin and cadmium. In addition, they made a limited study of deposition of films from solutions of salts of iron, cobalt, and nickel. Their best films were formed from solutions of stannic chloride and cadmium formate. With cadmium formate they were able to reduce the curing temperature to 250 C (418 F) the lowest temperature which they used.

Various additives were employed at both Battelle and Balco, in efforts to lower the resistances of the films. Balco found that the following additives lower the resistances of films formed from SnCl_4 : SnCl_2 , $\text{H}_2\text{N}\cdot\text{NH}_2\cdot\text{HCl}$, $\text{C}_6\text{H}_5\cdot\text{HN}\cdot\text{NH}_2\cdot\text{HCl}$, $\text{Na}_2\text{S}_2\text{O}_4$, SbCl_3 , TiCl_3 , and NaNO_3 . Battelle tried SnCl_2 , SbCl_3 , HF , and InCl_3 as additives to SnCl_4 , but there was too much scatter in the data to permit conclusions to be drawn on the effects of the additives. However, it was shown at Battelle that formation of a thin Sb_2O_3 overcoat on conducting SnO_2 films decreased the resistance of the SnO_2 film by a factor of 10. Balco also studied the use of additives in the formation of films from cadmium formate solution. They found that ferric, chromic, and thorium compounds increase the conductivity.

Balco studied the effect of baking time at 350 C (598 F) on the resistance of films formed from a stannous chloride solution. They found that a minimum resistance of about 1 megohm per square was attained after about 3 to 4 minutes of baking. Continued baking increased the resistance, and after 13 minutes the resistance was greater than 1000 megohms per square. Battelle made a similar study on films formed from stannic chloride solution and baked at 400 F. The average minimum resistance (about 15 megohms per square) was reached in about 1 day. After 7 days, the average resistance was about 200 megohms per square. The apparently different

results at Balco and Battelle do not necessarily conflict, since widely different curing temperatures were used, and since Balco used SnCl_2 , whereas Battelle used SnCl_4 . There is qualitative agreement, in the sense that both studies showed that a minimum resistance is reached, and that continued baking increases the resistance. In the Balco investigation, the minimum may have represented optimum proportions of stannous and stannic oxide (as a result of partial oxidation), since another investigation at Balco showed that films formed from mixed SnCl_4 - SnCl_2 solutions have minimum resistance when the concentration of SnCl_2 is about 3 to 5 per cent (based on the total tin content). However, the minimum in the resistance-baking time curve observed at Battelle probably is a result of some other effect, since SnCl_4 , rather than SnCl_2 , was used in the work.

Deposition of Films by Evaporation and Sputtering

Studies of formation of transparent conducting films by evaporation and sputtering at Battelle and Balco were entirely different. The Battelle investigation consisted primarily of evaporation of metallic films of tin and indium, with subsequent conversion to the oxides. Some preliminary studies on sputtering of indium and subsequent conversion to the oxide were carried out near the end of the contract period. On the other hand, Balco did only a small amount of exploratory work on evaporated films. Most of their work was on sputtering of cadmium, with sufficient oxygen present in the sputtering chamber so that cadmium oxide films were formed directly.

Since the Battelle and Balco evaporation and sputtering investigations were conducted along entirely different lines, and since the investigations are discussed in the final reports on the projects, it does not seem appropriate to present an additional detailed discussion in this report. However, Balco made some findings in connection with their cadmium sputtering which may be helpful in the future work at Battelle on indium, although sputtering of different materials presents different problems, and, therefore, may require the use of different techniques. The Balco findings are outlined below.

The Balco workers found that the best sputtering-gas composition for preparation of CdO films is 10 to 20 per cent oxygen in nitrogen. This is in contrast to the work of Helwig, who found that very low oxygen concentrations are required to obtain good film conductivity. The Balco workers also found that too high a concentration of oxygen causes the film resistance to be high, and that too low a concentration results in formation of metallic films. They tried adding water vapor to the sputtering gas to accelerate the sputtering, but found no appreciable effect. Use of water vapor alone as a sputtering atmosphere resulted in incompletely oxidized films.

Investigation of the effects of other sputtering parameters disclosed the following facts.

- (1) Higher current densities give films with higher conductivity and transparency.
- (2) A cathode-substrate distance of 11 millimeters gives maximum density of deposition. There is little variation in film resistance for spacings from 7 to 16 millimeters, or in sputtering rate for spacings of 8 to 16 millimeters.
- (3) With an uncooled cathode, the temperature of the cathode rises continuously during sputtering. As a result, the cathode tarnishes and begins to arc; also, the films become more metallic. Cooling the cathode with water eliminates these effects.
- (4) Conductivity of the films is dependent on the temperature of the substrate during deposition, higher temperatures resulting in higher conductivities.
- (5) The substrate composition affects the film characteristics. Sputtered CdO films on acrylic plastic are nonadherent and nonconducting. Undercoating with SiO_2 permits formation of CdO films with low resistance and good adherence, whereas with an undercoat of TiO_2 the CdO films are nonconducting.